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PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. L. H. Appleby has returned from Persia.

Mr. C. E. Capito has returned to Trinidad.

Mr. L. V. A. Fowle has left for Iraq.

Mr. F. E. Hunter has returned from Rumania.

Mr. H. M. Sale has returned to India.

Mr. L. C. Stevens has left Rumania and is in Trinidad.

Mr. G. Stewart Taitt is in Holland.

The Secretary would be glad to hear of the whereabouts of the following members:—E. E. G. Agius, T. E. Beaumont, G. Bourkoff, A. F. Brown, S. O. Connor, A. E. C. Corbet, A. R. Crawford, E. H. Crush, J. Dalgleish, W. H. Farrand, W. M. Gray, T. B. C. Harris, E. J. D. Hewitt, L. B. Holloway, P. N. Hulme, A. MacLean, J. McWilliams, R. E. Palmer, A. Rauch, and L. N. White.

OBITUARY.

Dr. SIDNEY POWERS.

On November 5th, 1932, one of America's most distinguished Petroleum Geologists, Dr. Sidney Powers, passed away consequent upon an operation. Only 42 years of age, Dr. Powers has been cut off in the prime of life, and only those who knew him, who were aware of what he had already done, and what he might have accomplished had he been spared, can evaluate the loss Petroleum Technology has suffered by his premature death.

Dr. Powers was born at Troy, N.Y., on September 10th, 1890. He had a distinguished academic career, first at the Massachusetts Institute of Technology and later at Harvard University. At the former he gained the Sheldon Travelling Fellowship, which enabled him to carry on his studies outside of the United States, while he gained a research fellowship at Harvard, obtaining his Ph.D. in 1915. In the following year he obtained a position as geologist with the Texas Company, which he relinquished to take up an appointment as Assistant Geologist on the U.S. Geological Survey. In 1919 he became chief of the geological staff of the Amerada Company, and was still consulting geologist to that company at the time of his death.

Dr. Powers was an active member of various geological societies and institutions, was elected President of the American Association of Petroleum Geologists for the term 1930–31, and was also a member of our own Institution, in which he took a greater interest than many of us could be aware. His contributions to geological literature were numerous and covered a wide field. His work is to be found in many American journals, amongst the Bulletins of the U.S. Geological Survey, while he contributed also to our own Symposium on Salt Domes. His aptitude for obtaining geological information and data was remarkable. His papers on " Buried Ridges " and his more recent work in connection with the Symposium on the " Occurrence of Petroleum in Igneous and Metamorphic Rocks," published as recently as August, 1932, in the Bulletin of the American Association of Petroleum Geologists, and of which he was Editor, provide ample proof of this. In addition, he was in the foremost rank as a reviewer of geological literature.

A man of the most kindly disposition, Dr. Powers was always considerate and helpful to all with whom he came in contact.

The younger generation of American geologists will greatly miss his influence, the fine example of his life and work and his freely given advice.

To his widow and family, to the American Association of Petroleum Geologists, and to his colleagues we tender our deepest sympathy. A. W.

LIBRARY.

The following additions have been made to the Library since November 1, 1932 :—

Casimir, Emil E. Studiul Titeiurilor din Regiunile Ochiuri, Baicoi, Tintea si Ceptura. Inst. Geol. Romaniei, Vol. XIII., Fas. 12.

Fuel Research Board. Survey Paper 25. The Yorkshire, Nottinghamshire and Derbyshire Coalfield. South Yorkshire Area. The Silkstone Seam.

Louisiana Dept. of Conservation. Geol. Bull. 2. Foraminifera of the Jackson Eocene at Danville Landing on the Ouachita, Catahoula Parish, Louisiana. H. V. Howe and W. E. Wallace.

Marek, L. F., and Dorothy A. Hahn. The Catalytic Oxidation of Organic Compounds in the Vapour Phase.

Thompson, A. Beeby. Emergency Water Supplies for Military, Agricultural and Colonial Purposes. (1924.)

U.S. Bureau of Mines. Repts. Invest. 3182. Review of Fatalities in the California Petroleum Industry during 1931. R. L. Marek.

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No. 110. Vol. 18.

The Physical Properties of Mixtures of Bitumen and Finely Divided Mineral Matter.*

By A. Evans, A.R.C.S., B.Sc., D.I.C. (Student Member).

General Introduction.

In this piece of research work the physical properties of mixtures of residual bitumens with various types of finely divided mineral matter, or "filler" as it is called, have been determined. Such mixtures of bitumen and filler, of suitable consistency, are frequently called "Asphaltic Cement" or "A. C." Owing to the fineness of division of the fillers and the consequent large total surface area per unit volume offered to the bitumen, fillers may be very intimately mixed with molten bitumens and the resulting material considered, from a mechanical point of view, almost as a simple substance or "bitumen-filler mortar."

Consequently it might be expected that the proportion and nature of the filler would be at least as important a factor in determining the properties of the A. C. as the properties of the bitumen itself; and, in view of the many uses to which asphaltic cements are put it would appear desirable to carry out determinations of the physical properties of various A. C.'s containing :—

1. Varying proportions of filler.
2. Fillers of different natures.

The systematic examination of asphaltic cements has not attracted many research workers, and consequently the literature contains very few references to such work.

Abrahams, in "Asphalts and Allied Substances," gives the results of some determinations of the physical properties of mixtures of precipitated chalk and Mexican residual bitumen. These figures show that :—

1. As the percentage of filler increases, the melting point rises, slowly at first and then more rapidly.
2. The penetration decreases fairly regularly over the whole range of mixtures used (the penetration is a measure of the hardness of an A. C., the lower the penetration the harder the A. C.).
3. The ductility decreases rapidly at first and then more slowly in the case of the mixtures made with the harder bitumen, while the ductility of the mixtures containing the softer decreases fairly regularly and to a much less pronounced degree.

* Paper awarded Students' Medal and Prize, 1931-1932.

H. Suida and *A. Schmolzer* (*Petr. Zeit.*, 1929, XXV., 251) describe experiments in which the properties of A. C.'s made from :—

Binder.

1. Trinidad asphalt.
2. Petroleum pitch.
3. Coal tar pitch.

Filler.

1. Powdered crystalline limestone.
2. Quartz.
3. Granite.
4. Brick dust.
5. Micro asbestos.

Curves showing the variation of flexual strength with filler content are given, and show very clearly the great increase in strength caused by the addition of micro-asbestos to the bituminous material, due to its fibrous nature, while the test results for quartz, granite and powdered crystalline limestone closely resembled one another and the brick dust mixtures gave very low results.

Hubbard and *Field* (Proc. A.S.T.M., 1930) show that the stability of an asphalt pavement is increased by the introduction of filler up to 25 per cent. It is also shown that hydrated lime is more efficient than limestone dust. This is probably because hydrated lime, being a chemical product, will be more finely divided, and in the form of spent carbide is used as a bitumen filler by certain steel pipe manufacturers to render bituminous pipe coatings less susceptible to temperature changes. Its appreciable solubility in water might, however, render it unsuitable for many bituminous compositions exposed to very wet conditions.

A. R. Ebberts (Roads and Road Construction, 1931) demonstrates the superiority of calcareous over siliceous fillers in paving mixtures. The former tend to form water in asphalt emulsions, while the latter give asphalt in water emulsions with consequent loss of asphalt by washing away with water (rain). These results were confirmed by tests on samples placed in running water, when it was found that A. C.'s containing siliceous filler lost more bitumen than the limestone mixtures. This is in accordance with practical experience that roads made with broken stone derived from " acid " igneous rocks rich in silica tend to peel off the tar or bitumen coating, while those made with " basic " rocks, such as basalt or limestone, show less tendency for the bitumen to be displaced by meteoric water. Nevertheless highly siliceous aggregates, such as

granite and sands, are commonly used in road making, on account of cheapness and of high crushing strength. Again, in the case of acid-resisting mastics, siliceous filler and aggregates must be used in order to attain the *maximum* degree of insolubility in acids.

Materials Used.

Three grades of bitumen were used in these tests :—

1. 40/50 penetration bitumen.
2. 60/70 penetration bitumen.
3. 190/210 penetration bitumen.

These bitumens were first tested in the usual way :—

1. *Penetration.*—This test was carried out in accordance with the method given in the Institution of Petroleum Technologists' book "Standard Methods of Testing Petroleum and its Products." An additional reading was taken, in the case of the 40/50-grade and 65 grade mixtures—namely, the penetration for a 60 second period with a 100 gram load ; the reason for this is given later, when the tests on the actual mixtures are described.

2. *Melting Point.*—This was determined by the standard I.P.T. apparatus.

3. *Ductility.*—The standard I.P.T. ductility machine was used and in addition to the usual reading, when the rate of pull is 5 cms./minute, a second reading was obtained, using an extension rate of 20 cms./minute.

4. *The Tensile Strengths* of the 40/50 grade bitumen, of the 65-grade and of one other bitumen of considerably lower penetration (Ebano Grade 1) were determined in a manner described later.

The results of the above tests carried out on material taken from the upper layers of an unused 2-gallon can of 40/50 penetration bitumen, which had been stored for about a year, with the top removed, show that the penetration has changed from 43 to 33, while the melting point and ductility are still within the specification limits.

An attempt was made to find the reason for this change in properties on storage. It was thought that perhaps the surface layers alone had undergone some change causing hardening. All three samples of bitumen had been stored for about a year, in a dark cupboard, in the 2-gallon cans in which the bitumen had been originally supplied and the tops of which had been removed shortly after their arrival. In order to see whether the hardening was confined to the surface layers, the latter was sampled to a depth of $\frac{1}{4}$ in. and the usual properties measured, including the ductility

at a rate of separation of the jaws of the moulds four times the standard 5 cms./minute, in order to bring the ductility values well within the range of the machine. It will be understood that the penetration of the surface layer of the stored bitumen was not determined by the direct application of the needle to the surface, but to a sample cut out and tested in the usual way. The amount of dust which is thus incorporated into the body of the bitumen is far too small a percentage to have an appreciable effect in reducing the penetration. The same tests were carried out on the bitumen from the body of the samples of the three grades of bitumen (at least 2 in. down) and the following results were obtained :—

TABLE I.

Bitumen.	Penetration. 5 secs.	Penetration. 60 secs.	Melting Point.	Ductility in cms. 5 cms./min.	Ductility in cms. 20 cms./min.
40/50—Surface ..	28	—	59° C.	+110	22
Body	42	95	55° C.	+100	95
Original	43	—	55° C.	+100	—
"65."—Surface ..	36	93	56° C.	+100	+100
Body ..	42	178	52° C.	+100	+100
Original ..	58	—	52° C.	+100	—
190/210—Surface ..	136	—	41° C.	+100	+100
Body ..	198	—	38° C.	+100	+100
Original ..	204	—	38° C.	+100	—

It is thus evident that the surface layer has, in each case, hardened in some way during standing. This phenomenon has been observed by several investigators :—[1, 2, 3, 4, 5]

The results in Table I. for 40/50 grade bitumen agree well with the figures given by Speilmann. It has been suggested that the hardening is due to oxidation, the action of light and polymerisation. In this case the bitumens were not subjected to the action of light during storage, so that the hardening was most probably due to polymerisation and, perhaps, to oxidation. As an investigation into the causes of the spontaneous hardening of bitumen samples on storage did not form part of the original scheme of this research, the matter was not pursued any further, but it is obvious that this is an important consideration when comparing the properties of samples of bitumen-filler mixtures stored over periods of several months or more.

The 190/210 penetration bitumen, from a depth of 2 in. to the bottom of the sample container, showed only a small percentage drop in penetration from the original figure, and was within the normal

[1] Dow. *Proc. A.S.T.M.*, 1903, **3**, 349.
[2] Hubbard and Reeve. *Ind. Eng. Chem.*, 1913, **5**, 15.
[3] Church and Weiss. *Proc., A.S.T.M.*, 1915, **15** (II), 274.
[4] Reeve and Lewis. Ibid., 1917, **9**, 743.
[5] Speilman, "Bituminous Substances," 1925, 72.

specification limits of 190/210, but, curiously enough, the 65-grade showed a marked hardening even in the body of the bitumen, and the test result was well outside the specification limit.

Accordingly, a fresh sample was obtained, giving the following test results :—

TABLE II.

Penetration, 5-second period	63·5
Penetration, 60-second period	177
Melting Point	121° F.
Ductility 5 cms./minute	+100 cms.
Ductility 20 cms./minute	+100 cms.

The following is a list of the fillers used :—

1. " Semi-Colloidal Silica."
2. Portland cement, normal grade.
3. Portland cement, from the air separator.
4. Ground chalk.
5. Ground limestone, original sample O.
6. Ground limestone, 200 mesh, screened from 5.
7. Ground limestone, 120/200 mesh, screened from 5.
8. Micro-Asbestos.
9. Slate dust.
10. Mineral filler from Trinidad Lake Asphalt.

These fillers were all dried in an electric oven at 110° C. before use, and then stored in dry, wide-necked bottles, fitted with ground glass stoppers. Over 85 per cent. of all the fillers passed the 200 mesh screen except 5, of which 66 per cent. passed this screen.

The size of the micro-asbestos particles was determined by means of a microscope fitted with a reticule. The lengths of the smallest and largest fibres observed were 0·016 mm. (0·0006 in.) and 0·4 mm. (0·016 in.) respectively. The lengths of the large majority of the fibres lay between the limits 0·04 mm. (0·0016 in.) and 0·08 mm. (0·0032 in.).

By the term " Filler " is understood very finely divided (but not necessarily impalpable) solid matter, which is insoluble in water and in bitumen solvents, such as carbon disulphide, and which can be blended with molten bitumen by stirring at suitable temperatures until a homogeneous mixture is obtained.

APPARATUS AND TESTS.

The tests carried out on each mixture were, melting point (Ring and Ball), penetration at 77° F., ductility at 77° F. and tensile strength at 77° F.

1. *Melting Point.*—The Ring and Ball method (the I.P.T. standard) was used. The rings containing the samples were cooled down to at least 10° C. for 15 minutes, when testing mixtures containing 190/210 penetration grade; but in the case of the 40/50 grade and the 65 penetration grade mixtures, the initial cooling to 5° C. for 15 minutes was found to have no effect on the melting point obtained, and so the samples were placed for 10 minutes in water at 15° C. or less before commencing the actual test.

2. *Penetration.*—The method described in the I.P.T. Book of Standard Methods was used, but in addition, in a few cases, the procedure adopted by Coomber at the suggestion of Prof. Illing was employed. For this purpose penetration dishes with removable amalgamated bottoms were used. These enable the penetration to be carried out on the bottom as well as the top of the material in the dish, after the bottom plate has been removed. Any settling of filler is then detected by the bottom of the A.C. giving lower pentration values. Two penetration values were taken for each mixture, one being the standard value for a 5-second period, and the other for a 60-second period, each with a 100 gram load. In this way two curves were obtained for each mixture, giving a double check on the values found, and also the 60-second penetration has a smaller percentage error, especially in the case of the harder mixtures, for which the 5-second penetration value is very low.

3. *Ductility.*—For this the Standard I.P.T. Ductility Test was used. In the earlier experiments, the bath was maintained at the standard temperature of 25° C. (77° F.) by means of five small gas jets, which heated a large sheet of tin plate, separated from the bottom of the bath by a space of about ½ in. Thus the bath was virtually heated by an air bath. The gas supply was regulated by a toluene-mercury regulator, and by this means it was possible to maintain the temperature of the bath at 25° C. ± 0·2°. Later, a steam heating coil was introduced under the porcelain plate, and the water stirred by means of a small mechanical stirrer. This was found to be a more convenient arrangement than the gas heating, as it was much easier to carry out ductility determinations at temperatures other than 25° C. Thus it was possible to raise the temperature of the bath comparatively rapidly, about 15° C. in 30 minutes as compared with three hours by the gas heating method. Cold water was passed through the coil in cases when it was necessary to carry out determinations at 60° F. or below.

Using the normal rate of pull (5 cms./minute), some of the mixtures, especially those of low filler content, gave very variable results—*e.g.*, one mixture gave values varying as much as 58 cms. and

100 cms. This may have been due to the fact that the thread became too thin before breaking, *i.e.*, of a diameter of the same order as that of the filler particles, when any local accumulation of filler would cause a weakness and consequent breaking of the thread before the true ductility value had been reached. In an attempt to overcome this, ductility tests were carried out, using a rate of pull of 20 cms./minute, the object being to break the thread when it was comparatively thick. This gave more consistent results in many cases—*e.g.*, the sample mentioned above gave 51, 61 and 63 as the ductility values when the rate of 20 cms./minute was used.

The above method is also useful for comparing the ductilities of pure bitumens, which give test results beyond the limits of the machine, when the standard 5 cms./minute rate is employed *i.e.*, ductilities of over 115 cms.

4. *Tensile Strength.*—This is not carried out as a standard test in this country, and as the actual determinations were made at a later date than the other tests, a description of the tensile strength test is given in a separate section.

The Preparation and Testing of the Mixtures.

With each bitumen five mixtures were made up, containing 12·5, 25, 37·5, 50 and 60 per cent. by weight of filler respectively. About 250 gms. of each mixture was made up and found to be sufficient for the tests carried out.

The maximum filler content in the bitumen-filler mixtures was fixed at 60 per cent. by weight, because this was found to be the limit of filler concentration which could be obtained by hand mixing in the case of those fillers (such as epure mineral matter, micro-asbestos and "Stockolite") which exhibited the highest degree of bitumen stiffening power.

The bitumen was weighed out, to the nearest gram, into an enamelled saucepan, having no sharp corners where the filler might collect and thereby reduce the weight of filler actually in the mixture. This was then clamped so that about $\frac{3}{4}$ of the pan was immersed in an oil bath which could be heated to any temperature up to 200° C. The temperature was adjusted to be about 70–80° C. above the melting point of the mixture being prepared. It was then possible to mix in the filler more evenly than when the bitumen was less viscous, when any small balls of filler were able to sink to the bottom of the pan and remain as nodules in the bituminous mass, thus making a mixture lacking homogeneity. When the mass is fairly stiff, these balls can be broken up by the stirrer before they sink. The maximum temperature to which any of the mixtures were heated was 100° C. above the ring and ball melting point.

When the bitumen was all sufficiently fluid, the filler was added in a slow thin stream and stirred in by means of a glass rod. The filler was contained in a funnel, clamped with the end of the stem about 1½ in. above the surface of the bitumen in the pan. If the filler had to fall through too great a distance, the finest part was apt to be lost into the air in the form of a cloud. The filler did not run through the stem of the funnel of its own accord, so a piece of stout iron wire, round which a thinner copper wire had been wound in the form of a spiral, was placed with its lower end in the stem of the funnel. When this was rotated, by means of a small electric motor, the filler was fed down the stem and on to the bitumen in a slow stream. The time of mixing varied, from 10 minutes in the case of mixtures of low filler content to an hour or more for those mixtures of high filler content.

In every case the time of mixing (*i.e.*, the time of heating) was kept as short as possible, to reduce the hardening of the bitumen due to loss of volatiles and/or oxidation and polymerisation to a minimum. The 90/50 penetration bitumen, when heated for 5 hours at 325° F., only hardens about 1 or 2 points, so that, during the time of mixing, the amount of hardening at about this temperature would be very small. At 400° F., however, the mixing period should be as short as possible.

When all the filler had been incorporated, the mixture was stirred for a further 10 minutes, to ensure homogeneity, and then poured into seven ductility moulds and two melting point rings, standing on an amalgamated plate and into a penetration dish. The melting point rings and the ductility moulds were allowed to cool for 30 minutes at room temperature, and then the surface of the bitumen in each was cut level by means of a hot knife.

The penetration dish, however, was first placed in an air oven for ½ hour, at a maximum temperature of 100° C. above the melting point of the mixture. This re-heating was found to be necessary in order to obtain consistent results. During the heating the mixture was stirred several times to prevent settling out of the filler, which is comparatively rapid at this temperature, for certain of the fillers, such as Portland cement. After the heating the tin was allowed to cool for one hour in a dust-free atmosphere, and then immersed for one hour in the water bath at 25° C. At the end of this time the tin was transferred to the penetrometer and the penetrations for the 5 and 60 second periods determined.

After levelling the A. C. surface, the melting point rings were mounted in the framework, which was then placed in the beaker containing water at 5–10° C. for the 190/210 penetration bitumen mixtures and at 10–15° C. for the others, and allowed to stand for 15 minutes before carrying out the test.

The ductility moulds were placed in the constant temperature bath for 90 minutes before carrying out the test.

These tests were carried out on the whole series of mixtures. Curves were plotted showing the variation in the several properties with concentration of the filler in the case of the 40/50 penetration bitumen. In plotting the ductility curves the average of the readings for any one mixture was taken as the true ductility (if one of the four values obtained differed widely from the others, this was not used in calculating the average). The figures for mixtures of 40/50 penetration bitumen and "Stockolite" were obtained by Coomber, working in this laboratory, and those for the precipitated chalk mixtures are taken from "Asphalts and Allied Substances" by Abrahams.

On examination of the curves (Figs. 1–3) it was found that, as the percentage of filler increased :—

1. The melting point (Fig. 3) increases, very slowly at first, and then, after 40 per cent., very rapidly and continuously to the maximum filler content, which it was found possible to incorporate in the bitumen without undue stiffness of the mixture and consequent difficulty in handling. The melting point of mixtures containing the cheaper fillers—*i.e.*, all those tested except epure mineral matter, micro-asbestos and very finely divided china clay—are about the same, and differ very little from the melting point of the neat bitumen, up to mixtures containing about 35 per cent. filler, when wide divergence begins.

2. The penetration (60 sec. period) (Fig. 1) decreases regularly ; there are a few irregularities, however, probably due to experimental error.

The two sets of curves give the fillers in approximately the same order of efficiency.

During the period of heating the penetration dish containing the sample, settling out of the filler may occur to an appreciable extent. In order to test for this, penetration tests were carried out on the top and the bottom of a sample. The bottom of a penetration dish was removed and the cylinder so formed stood on an amalgamated plate. The mixture was poured into this container and then treated as in the ordinary tests. After cooling, penetration tests were carried out on the top and the bottom of the sample :—

An A.C. containing 62·5 per cent. of 65 penetration bitumen and 37·5 per cent. Portland cement, gave a penetration of 48½ at the top and 47½ at the bottom.

These figures show that very little settling has taken place.

3. The ductility decreases, rapidly at first and then more slowly (Fig. 2). In some cases, notably ground chalk, semi-colloidal silica and Portland cement, a portion of the curve, over the range 20–40 per cent. by weight of filler, shows a tendency to flatten out, but the general shape of the curves is hyperbolic.

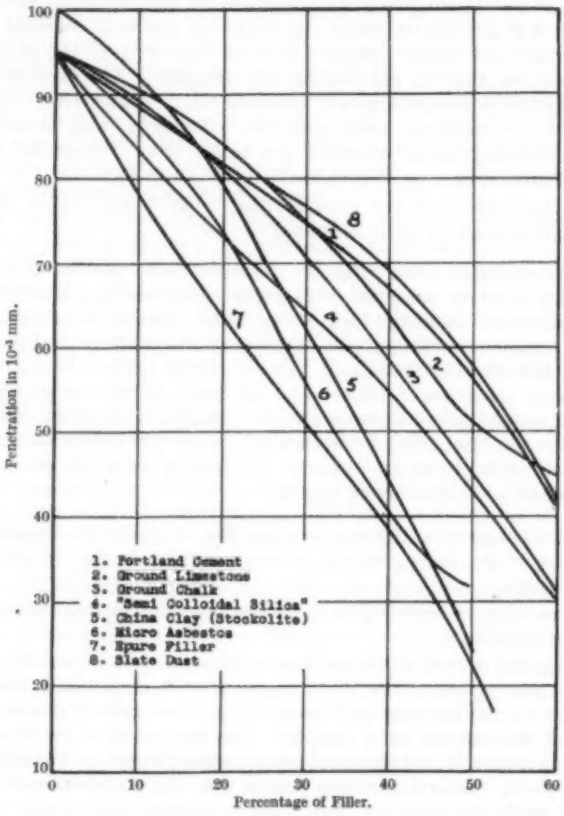

FIG. 1.

PENETRATION CURVES.

The ductilities obtained with the 20 cms./minute rate of pull are approximately one-half of the values obtained with the 5 cms./minute rate for mixtures containing 40/50 penetration

bitumen. This ratio for mixtures made with 65 penetration bitumen is about 0·6–0·7, while for 190/210 penetration bitumen mixtures the two ductility values are about equal; in fact, in some cases the ductility obtained with the faster rate of pull was greater than the value obtained when using the normal, 5 cms./min., rate.

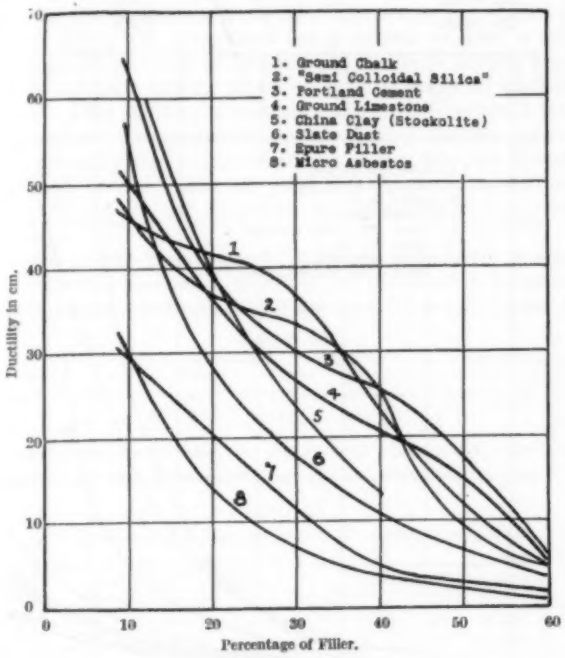

FIG. 2.

DUCTILITY CURVES.

The ductility figures obtained for any one mixture vary widely, and an attempt was made to see whether the variation was due to imperfect mixing of the filler and consequent lack of homogeneity. In order to determine whether this was the case, the thin part of the thread, obtained during a ductility test, was carefully dried and weighed in a platinum basin. The bitumen was then burned off, the basin ignited to constant weight and the percentage of ash calculated. This figure will be proportional to the percentage of filler in the mixture.

Sample Tested.—A.C. containing 87.5 per cent. 40/50 penetration bitumen and 12·5 per cent. Portland cement.

Ductility value obtained. Rate 20 cms./min.	Per centage by weight of residue on ignition of the material from the thin part of the thread.
51 cms.	13·3
36 cms.	13·3

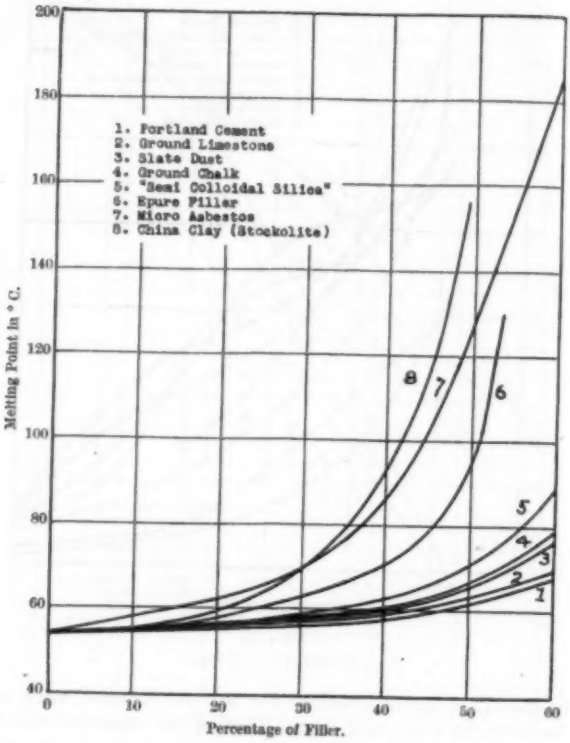

FIG. 3.

MELTING POINT CURVES.

The percentage by weight of residue in the material taken from end of the mould is 13·2.

These figures show that there is very little variation of filler content in the thin part of the thread, nor did this differ from the

filler content of the material comprising the bulk of the mixture in the mould. Even this did not give much information as to the filler content at the actual point of fracture, and, owing to the fineness of the thread, this value could not be obtained by ashing.

The ash value is higher than the original percentage of cement put into the mixture. In order to see whether this was an error in making up the mixture, cement and bitumen were weighed into a platinum basin, the quantities being chosen to give a mixture containing 12·5 per cent. of cement, and the basin heated, gently at first with constant stirring and then more strongly to burn off the bitumen. After igniting to constant weight, it was found that the ash percentage was greater than the original cement percentage. This is probably due to the sintering of the ash and the glazing over of the carbon; and the high ash figures obtained for the ductility thread are not, therefore, an indication of faulty cement percentage.

In order to check the reproducibility of the results, a complete repeat test was run on a blend of 65 penetration bitumen and Portland cement, containing 12·5 per cent. by weight of the latter.

TABLE III.

Sample.	Penetration. 5 secs.	Penetration. 60 secs.	Melting Point.	Ductility in cms. 5 cms./min.	Ductility in cms. 20 cms./min.
Original	61	173	51° C.	68	44
Repeat	62	169	51½ °C.	70	45

These figures show that the results are reasonably reproducible. The results for the above tests are given below :—

TABLE IV.

Properties of A.C.'s containing 65-Penetration Bitumen.

Filler.	Percentage of filler.	Penetration 5 secs.	Penetration 60 secs.	Melting point (in ° C.)		Ductility (at 77° F.) in cm. 5 cm./min.				Av.	20 cm./min.			Av.
Ground chalk.	12·5	56	155	51	51	58	70	73	100	80	51	61	65	62
	25·0	51	140	52	52	50	61	73	76	70	47	48	64	48
	37·5	40	112	54½	54½	50	52	61	73	51	28	30	33	31
	50·0	32	78	60½	60½	27	30	32	33	31	16	19	19	18
	60·0	23½	52	72½	72½	7	8	9	—	8	4	4	4	4
Semi-colloidal silica.	12·5	58½	159	51½	51	73	85	86	90	87	50	56	71	69
	25·0	47	132	53	53	52	59	59	70	57	42	43	46	44
	37·5	40	106	55½	55	44	49	54	55	50	30	32	38	33
	50·0	31	72	62½	62½	24	24	27	—	25	10	11	12½	11
	60·0	25	50	79	79	6	7	7	—	7	4	4	4	4
Portland cement normal grade.	12·5	61	177	50½	50½	58	66	69	74	68	41	42	47	44
	25·0	56	152	53	53	42	43	44	—	43	36	39	41	39
	37·5	49	141	54	54	31	32	34	37	34	26	26	27	26
	50·0	44	116	55½	55½	22	22	23	24	23	14	14	15	14
	60·0	36	87	60	60	10	11	11	12	11	5	6	6	6
Portland cement from air-separator.	12·5	60	173	51	51	74	76	83	—	77	60	83	83	83
	25·0	56	149	52½	52½	46	58	68	76	62	45	54	56	55
	37·5	54	143	54	54	35	39	40	46	40	24	26	28	26
	50·0	44	109	57	57	24	25	26	30	25	14	14	15	14
	60·0	32	72	63	63	17	18	20	—	18	5	5	6	6

TABLE V.

Properties of A.C.'s containing 40/50 Penetration Bitumen.

Filler.	Percentage of filler.	Penetration 5 secs.	Penetration 60 secs.	Melting point (in ° C.)		Ductility (at 77° F.) in cm. 5 cm./min.				Av.	20 cm./min.			Av.
Epure-filler.	11·0	32	76	57½	57½	25	28	31	—	28	17	17	18	17
	27·0	25	54	63½	63½	14	16	18	10	17	8	8	9	8
	36·3	20	42½	67½	68	6	6	7	—	6	4	4	—	4
	43·8	15	32	76	76	3½	3½	—	—	3½	2½	—	—	2½
	53·1	8	16½	133		2	2	—	—	2	—	—	—	—
Slate dust.	12·5	38½	88	57	57	36	45	45	—	45	20	21	18½	20
	25·0	33½	80	58	58	19	22	24	—	22	12	13½	13½	13
	37·5	30	73	61	61	13	13	15½	—	14	7	6	6	6
	50·0	24	57	66½	66½	6	6½	7	—	6½	4	3½	—	4
	60·0	21	41	77	77	3	—	—	—	3	2	—	—	2
Ground limestone —200 mesh.	12·5	38	89	57	57	43	45	48	—	45	23	26	28	26
	25·0	32½	79	57	57½	29	30	33	—	31	17	19	20	19
	37·5	29	67	60½	60½	15	21	29	—	22	11	12	12	12
	50·0	26	50	63	63	14	15	—	—	15	6	6½	—	6½
	60·0	21	44	69½	69½	5	4½	—	—	5	3	—	—	3
Ground limestone sample O.	12·5	40	94	57	57	32	35	37	—	35	18	19	20	19
	25·0	36	87	57½	57½	21	27	29	—	28	13	14	15½	14
	37·5	32	77	58½	59	12	16	17½	—	16	8	10	11	10
	50·0	28	62	61	61	8	11½	—	—	10	4	5½	—	5
	60·0	25½	50½	65	65	3½	4	—	—	4	2½	—	—	2½
Ground limestone —120 +200.	12·5	38	94	55	55	20	24	31	—	25	18	19	—	19
	25·0	36	84	56	56	20	23	—	—	22	13	13½	—	13
	37·5	33	67	58½	58	17	16	—	—	17	9	—	—	9
	50·0	30	58	62	62	7	—	—	—	7	4	—	—	4
	60·0	23	44	65	65	2½	—	—	—	2½	2½	—	—	2½
Micro-asbestos.	12·5	34	84	58½	58½	23	25	26	—	25	13	16	16	15
	25·0	30	66	64½	64	7	8	9	—	8	4½	4½	5	5
	37·5	20	41	80	80	4½	4½	—	—	4½	2½	2½	—	2½
	50·0	10	31	128		2½	—	—	—	2½	1½	—	—	1½
	60·0	—	—	190		—	—	—	—	—	—	—	—	—
Ground chalk.	12·5	34½	87	58	58	33	43	43	44	43	23	23	24	23
	25·0	30½	75	59½	59½	29	36	40	42	39	19	20	21	20
	37·5	25½	61	61½	61½	26	27	27	30	27	12	17	19	16
	50·0	21	45	67	67	11	11	12	12	12	4	5	6	5
	60·0	15	31	79	79	4	4	4	4	4	2½	2½	2½	2½
Semi-colloidal silica.	12·5	33	80	58	58	40	41	43	44	42	22	22	—	22
	25·0	29	68	60	60	29	34	35	40	34	19	20	—	20
	37·5	25	58	61	61	26	27	31	32	29	10	12	—	11
	50·0	17½	42	71	71	7	8	9	9	8	4	5	—	5
	60·0	13	30	90	90	4	4	—	—	4	—	—	—	—
Portland cement normal grade.	12·5	33	88	56½	56½	48	60	66	77	63	24	28	30	29
	25·0	29½	77	58	58	27	32	35	39	33	15	16	17½	16
	37·5	27½	69	58½	59	25	27	28	30	28	11	12	13	12
	50·0	24½	56	61½	61½	17	17	17	20	17	6	6	6	6
	60·0	17½	41½	66½	66½	6	6	6	—	6	3	3	3½	3
Portland cement from air se parator.	12·5	35	88	56	56	61	64	71	86	67	32	36	51	34
	25·0	30	78	57½	57	46	50	57	58	53	27	27	28	27
	37·5	27	65	60	60	27	29	30	35	30	12	14	18	15
	50·0	22	52	63	63	11	15	16	18	15	5	6	6	6
	60·0	19	38	70	70	4	5	5	5	5	3	3	3	3
Stocko-lite.	12·5	35	89	58	58	58	58	59	69	59				
	25·0	33	71	61	61	23	30	31	35	30				
	37·5	23	49	84	84	14	14	15	17	15				
	50·0	14	24	158		—	—	—	—	—				

TABLE VI.

Properties of A.C.s containing 190/210 *Penetration Bitumen.*

Filler.	Percentage of filler.	Penetration, 5 secs.	Melting point (in ° C.)		Ductility (at 77° F.) in cm. 5 cm./min.				Av.	20 cm./min.			Av.
Ground limestone —200 mesh.	12·5	175	38½	39	35	38	39	41	39	43	45	48	45
	25·0	159	40	40	37	41	43	45	42	45	46	—	45½
	37·5	130	42½	42½	40	48	52	—	47	51	57	64	57
	50·0	101	46	46	41	45½	—	—	43	46	50	—	48
	60·0	76	52½	52	31	37	—	—	34	33	35	—	34
Groud limestone sample 0.	12·5	196	39½	39	38	43	45	46	43	38	40	46	41
	25·0	167	41	41	19	26	32	35	31	24	28	32	28
	37·5	153	42½	43	22	25	30	—	26	19	21	26	22
	50·0	120	43½	44½	20	24	—	—	22	19	23	—	21
	60·0	83½	48½	49	15	16½	—	—	16	16	—	—	16
Ground chalk.	12·5	176	39½	39½	75	77	75	83	78	99	108	108	108
	25·0	153	40½	40	58	59	62	—	60	74	81	100	78
	37·5	120	43½	43½	43	52	54	54	54	54	66	77	66
	50·0	87	48½	49	35	41	42	44	43	41	44	47	43
	60·0	62	61	61	19	22	24	—	21	20	20	21	20
Semi-colloidal silica.	12·5	166	40	40	over 100					over 100			
	25·0	144	40½	40½	over 100					87	66	—	77
	37·5	122	43½	44	68	70	92	—	69	51	57	60	56
	50·0	85	50	50	32	37	40	—	36	32	33	34	33
	60·0	61	68	68	14	16	18	—	16	12	12	13	12
Portland cement, normal grade.	12·5	184	38½	38	46	68	64	74	69	76	59	87	81
	25·0	159	40	40	29	36	53	57	55	44	57	59	58
	37·5	138	40½	40	49	50	66	—	50	37	41	53	44
	50·0	112	25½	46	42	43	48	49	46	37	37	42	39
	60·0	81	50½	50½	32	33	34	42	33	28	31	32	31
Portland cement from air-separator.	12·5	187	39½	39	67	67	69	—	68	78	83	88	83
	25·0	167	40½	41	55	56	60	60	58	54	59	61	60
	37·5	132	42½	42½	56	61	62	—	60	55	57	57	56
	50·0	110	45	45	32	45	47	48	46	34	41	41	41
	60·0	77	51½	51½	26	27	29	30	28	24	27	30	27
Stockolite.	12·5	174	42	42	over 100								
	25·0	123	47	47	46	50	52	60	52				
	37·5	89	80	80	16	16	18	19	18				
	50·0	45	151		—	—	—	—	—				

THE NATURALLY OCCURRING FILLER IN EPURE.

It has long been, and is still, maintained by certain asphalt technologists, that epure, fluxed to suitable penetration with flux oils or with softer bitumen, is found to be superior in practice to residual petroleum bitumens to which equivalent quantities of filler have been added (the penetration of the residual bitumen being chosen to give an A.C. of penetration similar to that of the fluxed epure). This superiority is held to be partly due to the fineness of the mineral matter in epure and to the intimacy of its admixture with the epure bitumen. The figures given in Clifford Richardson's "The Modern Asphalt Pavement" for the mesh composition of epure mineral matter (including grading tests by sedimentation of aqueous suspensions in the manner practised in soil examination) indicate, however, that the bulk of the epure mineral matter is not much finer than that of typical rock flours,

while at the same time it appears probable that modern mixing machinery can incorporate such fillers in bitumens as thoroughly as can be achieved by nature.

It would appear, therefore, that if fluxed epure is superior in certain respects to comparable artificial bitumen-filler mixtures, and if this superiority is largely due to the nature of the epure filler, the latter must have some affinity for bitumens which is not possessed by normal rock flour fillers. Thus epure filler may have distinct bitumen adsorptive properties similar to those of fullers earth and decolorising clays. An indication that this is the case was afforded by some tests carried out by Mr. N. G. Gullick at the suggestion of Mr. A. Wolf, who suspected that epure filler might show physico-chemical activity towards bitumen. In these tests it was found that the physical and mechanical properties of blends of equal weights of residual bitumen and decolorising clay were very similar to those of equal weights of the same bitumen and epure filler, both mixtures having considerably greater strength and melting point than ordinary rock flour filler and bitumen mixtures.

As there is considerable difference of opinion among both highway engineers and asphalt technologists concerning the relative merits of fluxed epure and "synthetic" bitumen-filler mixtures, it is obviously a matter of interest and practical importance to determine whether the alleged superiority of fluxed epure is indicated by physical and mechanical tests. It was decided to determine the properties of original and reconstituted epure and blends of epure filler with 40/50 penetration bitumen, comparing these with one another and with "synthetic" A.C.s.

The first important point to be settled is whether fillers comparable in fineness with epure filler can be artificially incorporated with bitumen as intimately as has been accomplished by nature in the case of epure itself. For this purpose, the penetration, ductility and melting point of a sample of epure were determined, the first two tests being carried out at 115° F. instead of 77° F., in order to give test figures sufficiently large to reduce the experimental error to reasonable proportions. All these three tests were now repeated on a sample of "reconstituted" epure, prepared by extracting the bitumen from a large sample of the original epure with benzene, recovering the bitumen from the solvent and then blending it with the debituminised filler by hand stirring at about 160° C. in the usual manner. The method adopted for the extraction of the epure bitumen was that developed by Prof. V. C. Illing and Mr. A. Wolf, and is published elsewhere. In this method the finest portions of the mineral matter are separated from the bitumen extract by centrifugal means, but the separation is not complete, inasmuch as the bitumen still contains a small

amount of extremely finely divided mineral matter as shown by its ash content. For the purpose of the experiment under consideration, it was not, however, considered necessary to obtain a complete separation of the bitumen and filler, as the latter was subsequently to be re-incorporated in the bitumen, and the proportion of filler still left in this was too small to affect its physical properties to a marked degree.

The percentage of ash yielded by epure, the bitumen extracted therefrom, and the filler after the removal of most of the bitumen, together with the corresponding filler percentages, are shown below :—

Ash value of epure	.. ..	36·8% = 44% filler.
Ash value of extracted bitumen	..	3·98% = 4·76% filler.
Ash value of extracted filler	..	84·5% = 99% filler.

It will be appreciated that epure filler, however carefully debituminised by extraction with CS_2 will suffer further loss in weight on ignition due to evolution of water of hydration from the clay silicates and the burning off of any free carbon and irreversibly adsorbed bitumen, insoluble in CS_2.

The artificial epure was made up in exactly the same way as the other mixtures and the properties determined as before.

TABLE VII.

	At 115° F. Penetration. 5 secs.	60 secs.	Ductility. 5 cms./min.	Melting point
Natural ..	9	22½	6 cms.	104° C.
Re-constituted	7	20	4 cms.	112° C.

It will be observed that the properties of the reconstituted epure are very similar to those of the original epure. The lower penetration and ductility and high melting point of the former are probably due to the unavoidable loss of volatile hydrocarbons which occurs when extracted epure is freed from the last traces of solvent, the separation of natural bitumens from associated mineral matter without appreciable hardening being always a difficult proceeding. The decrease in ductility may also be due to incomplete breaking up of the strongly caked filler removed from the bottoms of the centrifuge tubes.

From these results one may draw the general conclusion that, even by the rather crude and inefficient method of hand-mixing, almost as intimate a blend of filler and bitumen as occurs in nature can be obtained. The presumption is that epure filler can also be as readily mixed with other bitumens and that there is no special virtue in natural mixing.

It follows that if epure filler has any special bitumen stiffening properties, these should be exhibited when the filler is artificially incorporated in other bitumens such as 40/50 penetration bitumen.

An examination of the properties of a series of blends of epure filler and 40/50 penetration bitumen, and a comparison of these with other filler 40/50 penentration bitumen blends of similar filler content (see Table V.) showed that epure filler was very decidedly superior to ordinary fillers such as limestone flour and Portland cement for increasing the hardness, tensile strength and melting point of the resulting A. C.s. This was brought out particularly clearly when comparing the various percentage-filler/melting point curves.

When deducing the practical significance of these results from the curves, it must be born in mind, however, that in the case of epure the filler content is limited to a maximum of about 44 per cent. (the usually accepted figure for epure itself), and will, in fact, in the great majority of cases, be considerably below this value, owing to the necessity of softening it by blending it with flux oils or bitumens of much higher penetrations than epure bitumen itself. The highest proportion of filler will be obtained when flux oil is used. A typical formula would be :—

Flux oil.. ..	15% by weight		
Epure	85% by weight	47·6%	bitumen
		37·4%	filler
	100%		

giving only 37·4% filler.

Consequently the lower strength-giving power of cheaper fillers such as limestone flour can be compensated for by increasing their proportion ; thus an A. C. containing 50 per cent. of –200 mesh limestone flour will have a somewhat higher tensile strength than an A. C. containing 35 per cent. of epure filler. There is, however, little doubt that by increasing the filler content of a fluxed epure to say 50 per cent. by the addition of extra filler, such as limestone flour, a blend would be obtained having a considerably higher tensile strength, etc., than an A. C. containing limestone alone, the penentration of the bitumen present being the same in each case.

The Effect of Particle Size on the Physical Properties of the A. C.

The researches on the properties of mixtures of certain bitumens with Portland cement and extremely finely divided china clay (carried out by Coomber, in this laboratory) seemed to indicate that an increase in fineness of the filler was accomplished by an

increase in the bitumen strengthening properties, the fine grade of Kaolin giving A. C.s of much lower penetration than the cement. It is true that, in this case, the particle shapes of the two fillers may have been different, and that they also differed in chemical composition, but there is a suggestion that fineness may be an important factor. Theoretically, one would expect an increase in fineness of the filler to be accompanied by a marked increase in the strength of A. C.s made with it, as the total surface area per unit weight of the filler will increase roughly as the square of the mean particle diameter, so that the total filler-bitumen interface, or contact area, will increase in like manner.

Theoretical considerations would also lead one to suppose that there is a limit to the degree of fineness desirable, for, if each particle of filler is to be surrounded by a bitumen film of definite thickness, a point will be reached when the surface area per unit weight of filler (and of bitumen) is so high that the amount of bitumen available becomes insufficient to coat the grains in the proper manner, and the proportion of filler has to be lowered. Also, the A.C. begins to lack the power of adhering to surfaces—*e.g.*, sand or roadstone when hot, because it is too dry and insufficient surplus bitumen is available to make a good bond at the stone A.C. interface. An excessively finely divided filler may be described as being "bitumen hungry" and, with normal bitumen contents, gives A.C.s and mastics which can only be spread with difficulty when applied to the surface to be covered at ordinary mastic laying temperatures. Practical experience gives ample evidence of this. It would appear preferable to select, when possible, those fillers which owe their bitumen strengthening power to their shape and/or adsorptive properties, rather than to their fineness of division, in all cases where the maximum proportion of filler relative to bitumen is to be used.

In order to discover the effect of the size of the filler particles on the properties of the A.C., two series of tests were carried out, using, this time, as filler :—

1. Two grades of Portland cement, one being the normal grade and the other a sample named "Portland cement collected in air separator," and considerably finer than the normal grade. The percentages passing the various mesh screens are given below :—

TABLE VIII.

	50/80.	80/120.	120/200.	−200.
Normal	0·2	0·9	10·6	88·0
"Air separator" ..	—	0·2	0·7	99·0

2. Three grades of limestone dust, the first being the original sample ; the second, the –200 mesh material screened from part of the original sample ; and the third, the 120/200 mesh fraction. The screening analysis of the original sample is as follows :—

TABLE IX.

Mesh size	30/50	50/80	80/120	120/200	– 200
% by weight passing screen	3·5	8·4	6·8	14·3	65·8

The bitumens used were 40/50 penetration bitumen and 190/210 penentration bitumen. Owing to the original supply of 42 penetration bitumen having become exhausted, the 120/200 mesh limestone –40/50 penentration bitumen mixtures had to be prepared with a new supply of 40/50 penetration bitumen, the penetration of which, although within the 40/50 range of this particular bitumen, was appreciably higher—viz., 46. Accordingly the penetration per cent. filler curves for the 120/200 mesh limestone have been based on penetration figures obtained by multiplying the observed penetration figures by the ratio 42/46. Even so, the 120/200 mesh limestone penetration curves may not be strictly comparable with those for the original and the –200 mesh limestone flour A.C.s. The results are given in Tables IV., V., VI., and those for 40/50 penentration bitumen and limestone are given in the form of graphs (Fig. 4).

These results, although not exhaustive, bring out the following points :—

1. The proportion of material passing the 200 mesh screen may vary from 60–100 per cent. without producing much alteration in the properties of the A.C.s within the range 0–60 per cent. filler content. This is especially noteworthy in view of the fact that the commercial tolerance in the penetration of a given bitumen at 77° F. may be as high as ±5 per cent.

2. The properties of mixtures made with 120/200 grade fillers would appear to be so near to the properties of the corresponding A.C.s made with the –200 mesh grade of the same filler that within the range of filler contents studied, the 120/200 mesh fraction of a rock flour or other aggregate would appear to be as much entitled to be considered filler as the –200 mesh fraction. This is important, as the question as to what proportion of the aggregate in a fine grained asphalt such as ground rock mastic shall be considered to be true filler is entirely arbitrary owing to the evenness of the grading. In asphalts, consisting of mixtures of sand, rock flour and bitumen, the difficulty of deciding which constituent shall be regarded as true filler is less pronounced owing to the unevenness of the grading.

3. If particle size is an important factor in determining the bitumen stiffening power of a given filler, this must refer to the proportion of extremely fine (say, 800 mesh) particles, rather than

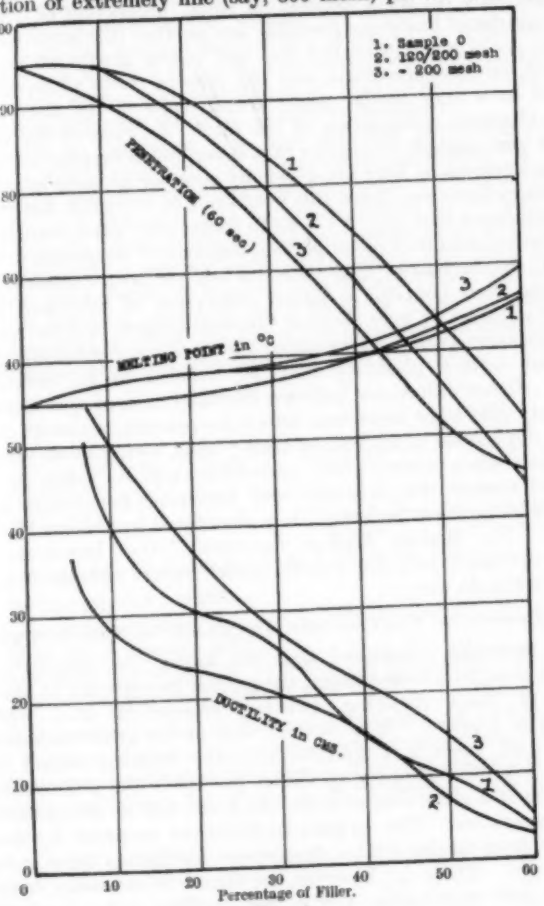

FIG. 4.

40/50 PEN. BITUMEN-GROUND LIMESTONE MIXTURES.

to the proportion of –200 mesh. In fact, two grades of a given filler may both pass the 200 screen completely, and thus be indistinguishable by ordinary screening methods and yet differ widely

in grading within the –200 mesh limit. A corresponding difference in bitumen stiffening power may then be expected.

4. Not only do A.C.s containing equal proportion of fine and coarse grades of limestone resemble one another (the same applying also to A.C.s made with the fine and coarse grades of Portland cement), but the limestone and the cement A.C.s of equal filler content have very similar properties, in spite of the dissimilarity in the chemical composition of the filler. In view of the experience of some asphalt companies that steam rolled carpets containing Portland cement as filler are decidedly superior to those containing the cheaper limestone flour, this would not be expected, but it must be remembered that only A.C.s up to 60 per cent. filler content have been studied, and that the important question of cementing power of the A.C. to the coarser aggregate has not yet been considered. If limestone flour contains a larger proportion of extremely finely divided particles, it may be more bitumen hungry, and the amount of free bitumen available for coating the coarser aggregate and giving the road surface plasticity may be reduced to an undesirable degree. Other differences between Portland cement and limestone flour may also have important effects in practice, although not so readily discernible in laboratory tests; thus, owing to its property of setting when moist, every precaution will be taken to keep Portland cement dry, whereas with limestone flour there is not the same inducement to do so. It is also stated by Clifford Richardson, in "The Modern Asphalt Pavement," that limestone flour A.C.s deteriorate in a few months under water, whereas Portland cement A.C.s do not.

The Effect of Varying the Ductility of the Bitumen.

It is generally considered that the higher the ductility of a bitumen at a given temperature, the greater its capacity to undergo change of shape (bending, twisting, elongation, etc.) without cracking or rupture. It is evident that in the great majority of, if not in all, cases it is desirable that the ductility should be as high as possible. Broadly speaking, the lower the penetration of a bitumen at a given temperature, the lower will be its ductility at that temperature. This applies to bitumens prepared by similar methods, from similar crudes, destructive distillation being avoided in all cases. There is, however, no direct relationship between ductility and penetration, and as the ductility is apt to decrease much more rapidly than the penetration if the bitumen has previously been heated to temperatures at which incipient decomposition takes place, it is obviously advisable to determine the ductility as well as the penetration of bitumens, whose quality is to be assessed.

The question arises, however, in view of the fact that bitumens are generally blended with fillers before use and that the addition of even a moderate proportion of filler reduces the ductility of the bitumen to a marked degree, whether the ductility of the bitumen itself is much of a guide to the ductility of the A.C. If for example, two bitumens A and B, of similar penetration but different ductility, are blended with equal proportions of filler, will the bitumen of higher ductility give the A.C. of higher ductility ?

In order to determine this, two different petroleum residual bitumens were fluxed with oil to the same penetration (at 77° F.) as the 40/50 penetration bitumen used for most of the bitumen-filler mixtures. One bitumen was purposely chosen to be very much harder than the other, in order to take advantage of the phenomenon well recognised in asphalt technology, that a very hard residual bitumen, when fluxed to a given penetration with a flux oil or a very soft bitumen, always gives a blend of lower ductility than when a somewhat softer bitumen is employed for the same purpose.

The properties of the two bitumens used are given below :—

TABLE X.

	Bl.	80/90.
Penetration at 77° F.	3	10
Melting Point (Ring & Ball) ..	265/285° F.	185° F.
Ductility at 77° F.	Nil.	Nil.
Solubility in CS_2	Over 95%	Over 99%
Type	Steam Refined Residual.	High Vacuum Distilled.

The properties of the flux oil used are given below :—

Specific gravity : 0·997.
Viscosity (Saybolt Furol) : 850/1200 secs. at 210° F.
Flash point (open) : 450° F.
Volatility loss at 325° F. (5 hours) : 1·0 per cent. max.
Type : Asphalt base residual road oil.

The properties of the two fluxed bitumens ; of blends of these with Portland cement and –200 mesh limestone dust ; and of 40/50 penetration bitumen and blends of 40/50 penetration bitumen with the same fillers, are shown in the following table :—

TABLE XI.

Bitumen.	0% filler.		25% Cement.		50% Cement.		25% Limestone.	
	Pen.	Duct.	Pen.	Duct.	Pen.	Duct.	Pen.	Duct.
40/50 Pen ..	41	100	29½	33	24½	17	27	20
Fluxed 80/90	41	75	31	13	23½	5	32	13
Fluxed Bl. ..	41	7	36	5	25	3	37½	5

Conclusions.—The ductilities of the neat bitumens would definitely appear to be a guide to the ductilities of the A.C.s prepared therefrom up to at least 50 per cent. by weight of filler, provided that

the latter is of such a character that the ductility of the A.C. is readily measurable. The quantitative value of the ductility test, when carried out on pure bitumens giving figures well over 100 cms., has been disputed by some asphalt technologists, because the bitumen is never required to form such lengthy threads in practice, and because when the thread becomes very lengthy, it also becomes so thin that variable results may be obtained.

The above examination of bitumen-filler mixtures does, however, appear to show that, bitumens having ductilities well over 100 cms. are distinctly superior to bitumens, having as high a ductility as 75 cms., for when sufficient filler is added to bring the ductility of the 100 bitumen, to between, say, 10 and 20 cms. (which is a very convenient range for observations, and usually gives readily reproducible results, owing to the thickness of the thread before breaking) the ductility of the +100 bitumen A.C. is seen to be more than three times as great as that of the 75 ductility bitumen A.C.

There would appear, therefore, to be a good deal to be said in the case of high ductility bitumens for standardising a ductility test on a carefully prepared mixture of equal parts by weight of bitumen and a given filler, rather than determining the ductility of the neat bitumen itself. The results thus obtained would be a valuable check on the variable figures often given by the bitumens of high ductility and would have a greater appearance to the practical man.

The Tensile Strength of Bitumen-Filler Mixtures.

As asphaltic cements are chiefly used for the purpose of cementing together aggregates coarser than the filler which they contain, it is obviously desirable that an A.C. should have as high a tensile strength as possible over the range of temperature to which it is exposed in practice. The tensile strength of pure residual bitumens rises to a maximum at a critical temperature, which is curiously enough generally coincident with the temperature at which the ductility approaches zero. For the bitumens normally employed, for paving, roofing, etc., this temperature is well below 60° F. The tensile strength of pure bitumens falls off even more rapidly than their hardness, with rise of temperature, and usually reaches the minimum figure, measurable with ordinary apparatus, when the ductility is at a maximum, and the softening point is nearly reached.

The tensile strength of pure residual bitumens, of medium penetration, is very low at 77° F. and blown bitumens are conspicuously deficient in this respect, even when of much lower penetration. One of the most important functions of a filler in A.C.s is to raise the tensile strength of the latter to a figure which may be several times that of the original bitumen. Other things being approximately equal, the best filler may be considered to be

the one which, for a given percentage, gives an A.C. of maximum strength at a given temperature. Broadly speaking, one might expect those fillers, which reduce the penetration and raise the melting point of a bitumen to the maximum degree, also to have the most pronounced effect in raising the tensile strength, although this does not follow in all cases.

The determination of the tensile strength of bitumens and A.C.s is not carried out as a standard test in this country, and no standard asphalt-testing instrument is available for the purpose. Accordingly a somewhat crude tensile strength tester was fitted up, based on the "Tensometer" described by Abrahams. For this purpose a spring balance, reading up to 100 lb., was inserted between the jaw of the ductility mould near to the fixed crossbar at the end of the tank of the ductility machine and the crossbar itself, the other jaw of the mould being attached to the moveable carriage in the usual manner.

With substances as ductile as A.C.s rich in bitumen the maximum reading given on the spring balance, when the two jaws of the mould are separated, will depend very largely on the rate of separation, being higher for higher rates. It is, therefore, essential when giving tensile strength figures, to state not only the temperature at which the test was carried out and the shape and initial cross section of the A.C. briquette, but also the rate of separation of the jaws of the mould, or the rate of increase of the load. In order to reduce the experimental error as far as possible, the jaws of the mould were separated as rapidly as manual operation of the machine allowed, viz., 25 cms. per minute. While the results thus obtained could not be directly compared with those given when other rates of separation of the mould jaws were used, they were reasonably consistent among themselves and afforded a valuable basis of comparison for the efficiency of the different fillers, from the point of view of raising the cohesive strength of bitumen and for ascertaining the effect of the tensile strength of the neat bitumen on that of the A.C.

The tensile strengths of a series of A.C.s containing 40/50 penetration bitumen and varying proportions of different fillers were determined at room temperature (about 70° F.) after the A.C. had been maintained in the mould for one hour at 77° F. Although the prevailing temperature of the laboratory was somewhat below 77° F., and the water bath of the ductility machine had been emptied (to avoid damaging the spring balance by immersion), since the test only requires a few seconds for its performance, it is unlikely that the figures obtained differ very much from those which would be given in water at 77° F. Each A.C. was tested

in duplicate, and the experimental error was of about the order ±5 per cent.

Had a more delicate spring balance, of narrower range, been

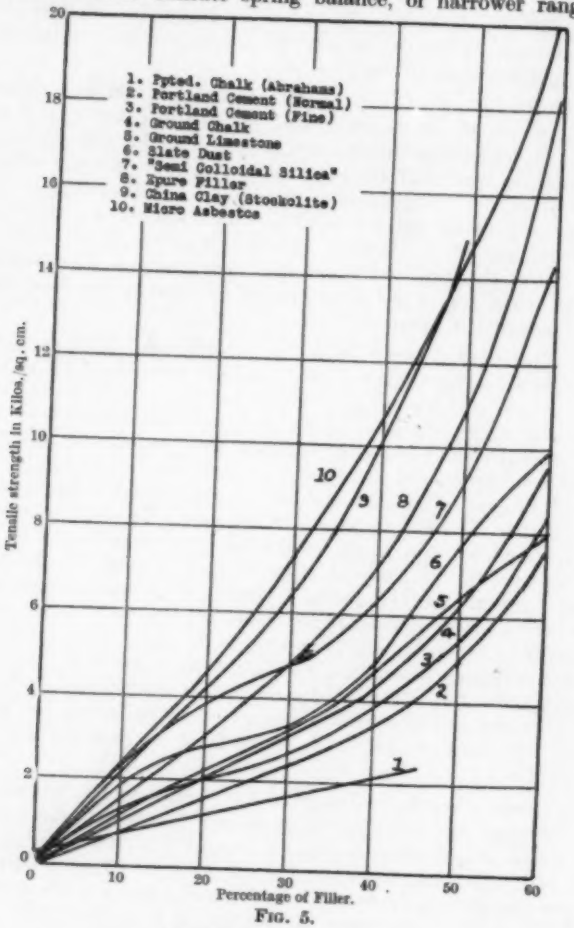

FIG. 5.

TENSILE STRENGTH CURVES.

available, the above experimental error might have been considerably reduced. However, the results obtained were sufficiently accurate, when plotted in the form of graphs (Fig. 5) showing the

variation of tensile strength with percentage filler, to bring out the following points:—

1. The tensile strength increases rapidly with the proportion of filler present.

2. Just as fillers differ markedly from one another in their power of increasing the melting point and hardness of A.C.s, so they differ in their power of increasing the tensile strength of the A.C. Very broadly speaking, the fillers may be placed in the same general order of efficiency in all three cases.

3. While the rate of decrease of ductility tends to fall off with increase in the proportion of filler, the reverse is the case with tensile strength, which is obviously advantageous from a practical point of view because A.C.s of high filler content are usually preferred.

4. Of the fillers commonly used for asphaltic cements, limestone flour is decidedly superior to Portland cement, up to 50 per cent. filler content, but thereafter Portland cement is superior. Slate dust and ground chalk give A.C.s of decidedly higher tensile strength than either cement or limestone flour for equal proportions of filler within the range tested. Epure filler is inferior only to the finest grade kaolin and micro-asbestos in its tensile strength raising power and, although normally limited to about 37 per cent. concentration would probably give better results than straight fillers in epure-flux-added-filler blends. Micro-asbestos, as one would expect from its fibrous structure, is remarkably efficient for increasing the tensile strength of A.C.s, being equalled in this respect only by the far more expensive "Stockolite" grade of China clay. The results concerning the efficiency of micro-asbestos agree well with the research on the flexural strength of A.C.s prepared with various fillers described in *Petr. Zeit.*, 1929, XXV., 251-254.

TABLE XII.

Tensile Strengths of 40/50 Penetration Bitumen and Filler Mixtures.

Filler.	K.gms./sq. cm. 12·5%.	25·0%.	37·5%.	50·0%.	60·0%.
Portland Cement (Normal) ..	0·9	2·1	3·0	4·8	7·5
Portland Cement (Fine) ..	1·6	2·3	3·4	5·2	8·4
Ground Chalk	1·4	2·9	3·8	6·1	9·3
Slate Dust	2·2	3·0	4·3	7·6	9·8
Colloidal Silica	2·8	4·3	5·7	9·3	14·1
Micro Asbestos	3·0	5·5	9·8	14·5	20·4
Kaolin	2·7	5·2	8·9	14·8	—
Ground Limestone —200 mesh	1·6	2·5	4·1	6·4	8·0
% of filler	11·0%	22·0%	35·0%	49·0%	60·0%
Epure filler	1·8	3·2	6·1	10·0	17·7

The Effect of Fineness of Division of the Filler on the Tensile Strength of the A.C.

It is significant that "Stockolite" and "Semi-Colloidal" silica, two of the most finely divided of the fillers used, also give A.C.s of highest tensile strength, but owing to difference in chemical composition (and presumably, also, in particle shape) no direct comparison on a fineness basis can be made between these and the other fillers. It is interesting to note, however, that the finer grade of cement, separated from the normal grade by air elutriation, gave a series of A.C.s of appreciably higher tensile strength than the normal cement A.C.s. This is in accordance with what one might expect.

The Relationship between the Penetration and Tensile Strengths of Bitumens, of Widely Varying Hardness, and of A.C.s Prepared with them.

It is obvious that the tensile strength of a hard or low penetration bitumen may be expected to be higher than that of a soft or high penetration bitumen and an examination of the table of properties of typical residual petroleum bitumens, facing page 343 in Asphalts and Allied Substances (1928 edition), shows this to be the case, the tensile strength varying (very roughly) directly as the hardness in the cases of those bitumens which have a reasonable ductility and a penetration not below about 10 at 77° F.

One would, of course, expect an A.C. containing a given percentage of a specified filler and made with a hard bitumen, to have a higher tensile strength than one otherwise similar, but prepared with a softer bitumen; but whether this is actually the case or not appears only to have been determined for precipitated chalk (Abrahams, page 398), a material which, on account of its cost, is not commonly employed as a filler for asphaltic compositions. For road, paving and building asphalts, where bitumens are always used in conjunction with filler, the tensile strength of the bitumen filler A.C. is of greater importance than that of the bitumen itself, and the question arises: "What increase in tensile strength is obtained by using a harder bitumen?" Accordingly the tensile strength of three typical bitumens, differing from one another in penetration and of three A.C.s made from these by mixing them with 66 per cent. by weight of fine limestone dust, were determined. The bitumens used were all petroleum residuals and were as follows:—

1. 60/70 *penetration Bitumen.*—Primarily used for steam rolled asphalt, either alone or blended with epure.

2. 40/50 *penetration Bitumen*.—Used for roofing and damp-coursing mastic asphalts, and for those flooring and paving mastics which are not subjected to heavy traffic.

3. 15/25 *penetration Bitumen*.—Primarily used for mastic asphalt paving and flooring, which is to be subjected to heavy traffic.

It may be observed here that softer grades of bitumen (such as 65 penentration) are frequently chosen for steam rolled work, because of their greater plasticity and ductility at low temperatures. In spite of the heavy traffic to which roads are subjected a relatively soft bitumen can be used (provided that the aggregate is correctly graded), because the load carrying capacity of the road is largely determined by the compaction of the coarser aggregate on rolling and the interlocking of the sand grains.

In mastic work such interlocking is not feasible, as the material must be spread under a hand float, and hence for heavy traffic harder bitumens than the above must be used.

The tensile strength of the pure bitumens were determined first and were, in the case of the two softer bitumens, found to be too low to give satisfactory readings on the 100 lb. balance. Accordingly, a second series of tests were carried out on the two softer bitumens using a 6 lb. spring balance. The results are given in the following table :—

TABLE XIII.

Bitumen.	Tensile strength on 6 lb. balance.	Tensile strength on 100 lb. balance.	Penetration at 77° F.
65 pen.	0·28 kilos.	—	65
40/50 pen.	0·86 kilos.	—	45
15/25 pen.	—	8·2 kilos.	19

From these results the following conclusions may be drawn :—

1. The tensile strengths of bitumens increase very rapidly with decrease in penetration and are not inversely proportional to the latter.

2. The tensile strength of a relatively hard bitumen of about 20 penetration at 77° F. may be as high as that of an A.C. containing as much as 60 per cent. by weight of cement or limestone flour, but made with a softer (45 pen.) bitumen (at the same time, the ductility of the 20 penetration bitumen at 77° F. will be superior to that of the A.C.).

It should be noted that the unexpectedly high tensile strength of the 20 penetration bitumen compared with that of the other bitumens may have been due to the fact that it was derived from a different type of crude, namely, from the Ebano field of N.E. Mexico. This crude is very heavily asphaltic, and contains a little wax as well as bitumen. In this respect it resembles Panuco

crude. The bitumen is characterised by having a relatively high viscosity at 200° C. The 45 and 65 penetration bitumens were obtained from the same or very similar types of crude, probably of Venezuelan origin.

The properties of the A.C.s made with the above bitumens were then determined. A limestone flour, of which over 90 per cent. passed a 200 mesh was chosen as a filler, owing to the frequency with which limestone flour is used as a filler in mastic and steam-rolled asphalts. As much as 66 per cent. of this was incorporated in the A.C.s, in order to obtain as high tensile strength readings as possible, and to approach the proportions frequently used in practice. The penetration and tensile strength of each A.C. at 77° F. was determined and the following results obtained :—

TABLE XIV.

Bitumen.	Pen. of Bitumen.	Pen. of A.C.	Tensile Strength of A.C.	Penetration Tensile Strength.
15/25 pen.	19	5	27·3 kilos.	136·5
40/50 pen.	45	17½	9·6 kilos.	168
65 Grade	65	27	5·5 kilos.	148

The above table brings out the following points :—

1. If the bitumens are placed in order of increasing tensile strength, the tensile strengths of the A.C.s fall in the same order but do not bear the same ratio to one another.

2. The difference between the tensile strengths of the A.C.s, although very marked, is not as great as the difference between the tensile strengths of the bitumens themselves.

3. The product of the tensile strengths and the penetrations of the A.C.s is approximately constant—*i.e.*, the tensile strength of an A.C. made with a given proportion of a given filler would appear to vary approximately as the hardness of the A.C., the changes being rung on the hardness of the bitumen only.

General Conclusion.—Where an asphalt is required to have maximum hardness and/or maximum tensile strength, it is advantageous to use, not only a filler of maximum strength giving properties, but also a hard bitumen, provided that the latter is not lacking in ductility.

CONCLUSIONS.

The researches carried out, although far from exhaustive, have already been sufficient to show that the physical and mechanical properties of asphaltic cements (and therefore presumably of the finished asphalts) are so profoundly affected by the nature and proportion of the filler used, that from a practical as well as from a purely scientific point of view it is at least essential to determine the properties of the A.C. as those of the bitumen itself. An

additional advantage gained by the examination of the A.C., as well as that of the bitumen itself, is that properties such as tensile strength and ductility, which when determined on the bitumen itself are often beyond the range of the instrument or subject to large experimental error, become much more convenient and accurate to determine. Thus ductilities can be reduced to low figures of greater practical significance as well as convenience, and the tensile strength can be raised to several kilos per sq. cm. even for quite soft bitumens.

A. Apart from questions of cost and availability, the choice of filler must depend largely on the balancing of various desirable properties of the A.C. It is, for example, very useful and instructive to arrange fillers in increasing order of tensile strength raising power, the efficiency of a filler in this respect being reckoned to be greater the smaller the proportion required to produce an A.C. of given tensile strength.

In the following table the fillers are arranged in decreasing order of the percentage required to give the A.C. a tensile strength arbitrarily fixed at 6 kilos (this corresponds with approximately 50 per cent. of an ordinary filler, when 45 penetration bitumen is used), and the ductility, penetration and melting point of each A.C. is also given :—

TABLE XV.

Filler.	% Filler to give tensile strength of 6	Ductility. 5 cms./min.	Penetration. 5 secs.	Penetration. 60 secs.	Melting Point.
Portland cement ..	55	12	22	49	63
" fine ..	53	12	21	49	65
Ground chalk ..	49·5	12	21·5	45	67
Ground limestone ..	48	16	26·5	52	62
Slate dust	44	10	26·5	55	63½
Colloidal silica ..	38·5	27·5	23·5	56	62
Epure filler	34·5	8	21	44·5	67
Stockolite	28·5	23	30	—	64
Micro-asbestos ..	26·5	7·5	29	63	65

The following points will be observed :—

1. The penetration and melting point are approximately constant.

2. The ductilities of the A.C.s prepared with the first five fillers are of the same order (ranging from 10–16). These are the cheaper fillers commonly employed in asphalts.

3. The use of a high efficiency filler results in an A.C. of either normal or alternatively exceptionally good or poor ductility.

B. It is important to determine whether, in the case of a series of A.C.s all containing the same proportion of a given bitumen, but made with different fillers, there is an approximate relationship

between the various properties of the A.C.s. In the following table are given the tensile strengths, melting point and penetration of such a series of A.C.s, each containing 50 per cent. by weight of 40/50 penetration bitumen, and arranged in increasing order of tensile strength. Also the ratio $\frac{\text{tensile strength}}{\text{melting point}}$, and the products, tensile strength × penetration (60 secs. period), and tensile strength × ductility, are inserted.

TABLE XVI.

Filler.	Tensile Strength.	Melting Point.	$\frac{\text{T.S.}}{\text{M. Pt.}}$	Pen. 60.	Pen. × T.S.	Duct. 5.	Duct. × T.S.
Portland cement ..	4·9	62	0·08	56	275	15	74
,, fine ..	5·3	63	0·08	52	276	15	80
Ground chalk	6·1	68	0·09	45	275	11½	70
Ground limestone ..	6·4	63	0·10	50	320	15	96
Slate dust	7·6	67	0·11	52	395	6½	49
Colloidal silica ..	9·5	71	0·13	42	391	8	74
Epure filler	10·4	93	0·11	23	239	2½	26
Micro-asbestos	14·5	127	0·11	31	450	2½	36
Stockolite	14·8	160	0·09	24	356	4	59

It will be seen that :—

1. The ratio tensile strength/melting point is of the same order in all cases. Now the melting point is a property which can be rapidly and easily determined with very simple apparatus, and is therefore of value, not only for indicating the upper temperature limits at which the A.C. begins to become too soft for use, but also as a rapid, approximate sorting test for arriving at the tensile strength of an A.C. It cannot safely be used in all cases, for work since carried out by other investigators has shown that ordinary scrap asbestos, for instance, while very inferior to micro-asbestos for increasing the tensile strength, gives A.C.s of remarkably high melting point.

2. Very broadly speaking, a filler which has a very pronounced hardening effect on A.C.s will also increase the tensile strength to a marked degree, but the product of the penetration and the tensile strength is far from uniform, inasmuch as it is found to vary from approximately 230–450 for the 50 per cent. filler content A.C.s examined. This is equivalent to saying that there is no constant relationship between the hardness of A.C.s of given filler content and their tensile strength, even if the same bitumen is used throughout.

3. The product of ductility and tensile strength, for a series of A.C.s containing 50 per cent. by weight of bitumen may vary between 26 and 96, showing that there is no simple relationship between ductility and tensile strength. The variations of T.S. × ductility also do not appear to bear any relationship to the

variations of tensile strength × penetration 60. Very broadly speaking, an A.C. of high tensile strength and low penetration will tend to have a relatively low ductility, whether the strength of the A.C. be due to hard bitumen or to high filler content, strength-giving filler, or to two or three of these factors combined.

C. In the following table the fillers examined are arranged in the orders of their melting point-raising, tensile-strength-increasing and penetration-decreasing (hardening) powers in columns 1, 2 and 3. In column 4 they are arranged in the order of their ductility-decreasing effect. Properties 1, 2 and 3 are obviously desirable, property 4 probably always undesirable, but nevertheless unavoidable.

TABLE XVII.

Order.	Increasing Melting Point.	Increasing Tensile Strength.	Decreasing Penetration.	Decreasing Ductility.
1.	Stockolite.	Stockolite.	Epure.	Asbestos.
2.	Asbestos.	Asbestos.	Stockolite.	Epure.
3.	Epure.	Epure.	Asbestos.	Stockolite.
4.	Silica.	Silica.	Silica.	Slate dust.
5.	Ground chalk.	Slate dust.	Ground chalk.	Silica.
6.	Slate dust.	Ground chalk.	Slate dust.	Ground chalk.
7.	Limestone.	Limestone.	Cement.	Limestone.
8.	Cement.	Cement.	Limestone.	Cement.

It will be noticed that in spite of the absence of any simple relationship between the various properties of the A.C.s, nevertheless the order of "efficiency" is about the same in all cases (all the A.C.s contained 50 per cent. of 45 penetration bitumen).

D. Test results quoted by Abrahams indicate that an A.C. of given penetration at 77° F. containing a soft bitumen and a relatively high proportion of filler will have a lower melting point, a lower ductility and a lower tensile strength than an A.C. of similar penetration at 77° F., but containing a harder bitumen and a lower proportion of filler. That this phenomenon applies (except with regard to melting point), even when the bitumens do not differ widely in penetration at 77° F., is well brought out in the following table :—

TABLE XVIII.

Filler.	% Filler		Melting Point		Ductility		Penetration 60.	
	E.	65.	E.	65.	E.	65.	E.	65.
Cement, normal..	11	60	56	60	60	11	87	87
Cement, fine ..	10	57	56	61	75	16	90	86
Ground chalk ..	10	43	57	56	46	42	89	97
Stockolite ..	9	26	57	63	95	44	93	91
Silica	7	44	57	58	58	40	85	89

It would appear preferable, therefore, when manufacturing an A.C. to use as hard a bitumen as possible (up to the limit when it shows poor ductility), and as low a proportion of filler as possible

to obtain the required strength and hardness and high melting point of the finished A.C. By doing so an A.C. of maximum ductility and tensile strength is obtained. There is the additional important advantage (not brought out by the test figures), that the A.C. prepared on these lines contains a large excess of bitumen available for cementing the A.C. to the grains of coarse aggregate, if the conditions of service demand that the A.C. be further strengthened and cheapened by the addition of such material.

GENERAL SUMMARY OF THE RELATIONSHIP BETWEEN THE PROPERTIES OF THE FILLERS AND OF THE BITUMENS, ON THE ONE HAND, AND ON THE OTHER SOME OF THE MOST IMPORTANT PROPERTIES OF THE A.C.s MADE BY BLENDING THESE FILLERS WITH BITUMEN.

A. The melting point, hardness and tensile strength are raised, and the ductility decreased by the following factors, two or more of which may operate simultaneously :—

1. Increase in the proportion of the filler.
2. Increase in the hardness of the bitumen.
3. Increase in the fineness of the filler.
4. Fibrous or lamellar as distinct from cubical structure of filler.
5. Increase in the bitumen adsorption power of the filler.

There appears to be no direct relationship between the chemical composition of the filler and the strength, etc., of the A.C. made therewith. This is similar to what occurs in the case of fullers earth and other decolourising powders, whose adsorptive properties appear to depend more upon their physical structure than upon their chemical composition.

B. The properties of the A.C.s are so much dependent upon the properties and nature of the filler that examination of the bitumen alone for hardness, etc., is not sufficiently informative.

C. Owing to the absence of any simple relationship between the penetration, ductility, tensile strength and melting point of A.C.s each of these properties must be determined if proper conclusions are to be arrived at concerning the suitability of the A.C. for a given purpose.

D. The ductilities of bitumens decrease to so marked a degree on the addition of fillers that the ductility of the original bitumen cannot be considered a guide to the ductility of the A.C. Broadly speaking, however, the higher the ductility of the bitumen (for a given penetration) the higher will be the ductility of the A.C. The very high ductility of certain grades of modern residual bitumens of high and medium penetrations (ductilities of over

115 cms. at 77° F.) is considered by some asphalt technologists as unnecessary, but it would appear that these high figures result in a definite improvement in the very much lower ductilities of the A.C.s rich in filler and may, therefore, be desirable. In this connection the penetration of the bitumen must be taken into account as the falling off in ductility on the addition of filler is much more marked in the case of lower penetration bitumens.

Perhaps the most important conclusion to be derived from this research is that unless the ratio of the proportion of filler to bitumen in asphalts is maintained within fairly narrow limits, it is impossible to manufacture asphalts of consistent properties however constant the proportion and properties of the bitumen itself. Thus, failure of asphalts, such as marking under heavy standing loads, traffic, etc., often ascribed to defects in the bitumen are really due to the use of an incorrect filler-bitumen ratio.

Acknowledgments.

In conclusion, the author wishes to tender his thanks to Prof. V. C. Illing, M.A., and to Mr. A. Wolf for advice, and unfailing interest throughout the work. Also, he is very much indebted to the courtesy of the following firms who supplied the materials used: Silica Industries, Ltd., Scott Bader, Ltd., British Portland Cement Manufacturers, Ltd., Imperial Chemical Industries, Ltd., and the Port Penrhyn Slate Quarries for fillers, and Shell Marketing Co., Ltd., Ebano Oil Co., Ltd., and the Texas Oil Co., Ltd., for bitumens and flux oils.

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Cements and Well Cementing: Effect of Chlorides on the Setting and Hardening of Cement.*

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Fluid cement introduced into a well may:—

1. Be diluted to a certain extent with underground waters; or
2. Set and harden under underground waters.

It is important to study the effect of these waters, more especially on the setting and hardening properties of cement. To obtain the fullest information, it is obviously best to study separately the effect of the individual constituents of the average well water; their conjoined effects may then be estimated.

In this work an attempt was made to study the effect of chlorides, which are present in the highest concentration in the average well water. Salinity is, in effect, frequently used as a means of identification of well waters of uncertain origin.

Occurrence of Chlorides in Well Waters.

The concentration of chlorides in well waters varies greatly. American authorities have reported salinities as high as 1500 parts of chloride per 100,000. The average well water, with which the authors are concerned, contains 350 parts Cl/100,000, corresponding roughly with a 0·6 per cent. sodium chloride solution. For this reason, in experiments involving temperature changes, the authors have used a 0·6 per cent. solution of sodium chloride.

Well-water chlorides are present almost entirely as the sodium salt. Potassium, magnesium and even calcium chlorides are found, but in such negligible proportions that it is considered their effects may be neglected. The authors have, therefore, considered the effects of sodium chloride alone.

The investigation may be divided into two main headings:—

1. Effect of chlorides on tensile strength of cement.
2. Effect of chlorides on setting time of cement.

Each heading is then capable of subdivision according to the conditions used in the various series of tests made. Thus experiments made under classification 1 may be further grouped under the following sections:—

(*a*) Cement grouted to 40 and 50 per cent. gauge with water containing various percentages of sodium chloride and cured under distilled water.

* Paper received October 21, 1932.

(*b*) Cement grouted to 40 and 50 per cent. gauge with distilled water, set under line water and then cured under 0·60 per cent. sodium chloride solution.

(*c*) Cement grouted to 40 and 50 per cent. gauge with distilled water and cured under 0·6 per cent. sodium chloride.

In the same way experiments made under classification 2 may be subdivided :—

(*a*) Cement grouted to 40, 50 and 60 per cent. gauge with water containing various percentages of sodium chloride, and allowed to set in moist air at a temperature of 100° F.

(*b*) Cement grouted to 40, 50 and 60 per cent. gauge with distilled water, and allowed to set under water containing various percentages of sodium chloride, the temperature being maintained at 100° F.

(*c*) Cement grouted to 40, 50 and 60 per cent. gauge with distilled water and allowed to set at various temperatures from 100° F.—160° F., under distilled water, and under 0·6 per cent. sodium chloride solution respectively.

Experimental.

It is not proposed to write much under this heading apart from indicating conditions employed and methods of testing used.

Cement.—A good-class grade of cement, manufactured specially for use in oil wells, was used throughout. The main characteristics of the cement are its property of fairly rapid hardening at comparatively high dilution and reasonably short setting under conditions of actual use.

Tensile Strength Tests.

Gauging.—40 and 50 per cent. grouts were used, the grouting media being either solutions containing 0·2, 0·4, 0·6, 0·8 or 1·0 per cent. sodium chloride or distilled water.

Curing.—Briquettes were cured either under distilled water or under 0·6 per cent. sodium chloride. In a third series (1(b.) above) the briquettes were grouted with distilled water, then placed under line water until they had attained the final set, and finally cured beneath 0·6 per cent. sodium chloride solution. Thus 1(b.) and 1(c.) give a comparison of the effect of 0·6 per cent. sodium chloride solution on cement which has set, and on freshly grouted unset cement. In actual practice this will be typified firstly by well water contacting with cement after the latter has been placed and has just taken its set; and, secondly, by well water contacting with the cement as it is placed (in the latter case we are ignoring the effects due to agitation or dilution of the grout by the well water).

Apparatus.—The rings used for holding the test pats were of B.S.S. pattern. All setting times reported were obtained with standard Vicat initial and final needles.

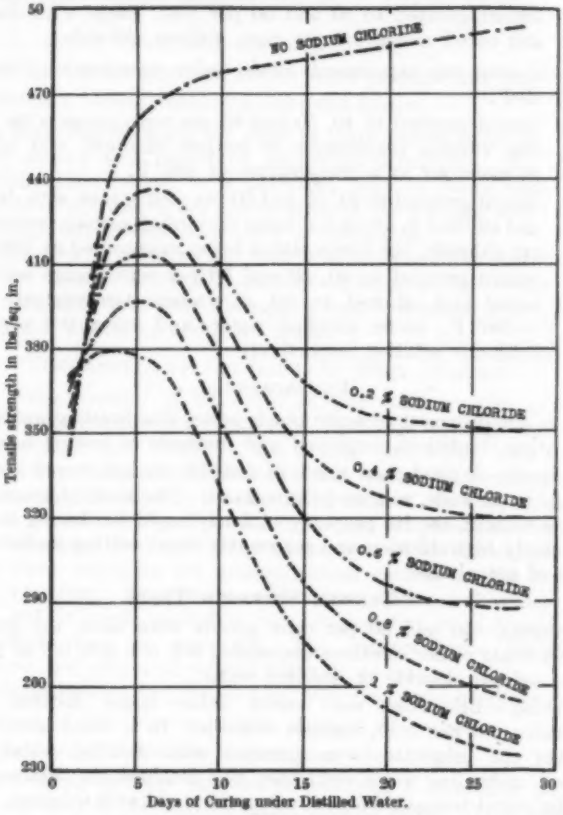

FIG. 1.

EFFECT OF SODIUM CHLORIDE SOLUTION ON THE TENSILE STRENGTH OF CEMENT (40 PER CENT. GAUGED WITH NaCl SOLUTION).

Temperature.—Excluding the tests listed under 2(c.) above, for the whole of the work dealt with in this report a thermostat at 100° F. was employed.

Confirmation of Results.—The standard procedure throughout was to obtain six results for each test—*i.e.*, for any given tensile

strength determination six briquettes were made up, and each setting time test was repeated six times. If it was considered desirable, further determinations were made; in general this was not necessary. The figures given in the tables are the averages of these determinations.

Discussion of Results. Tensile Strength Tests.—We shall consider first the effect of chlorides in the grouting water on tensile strength. The results for various percentages of sodium chloride in 40 and

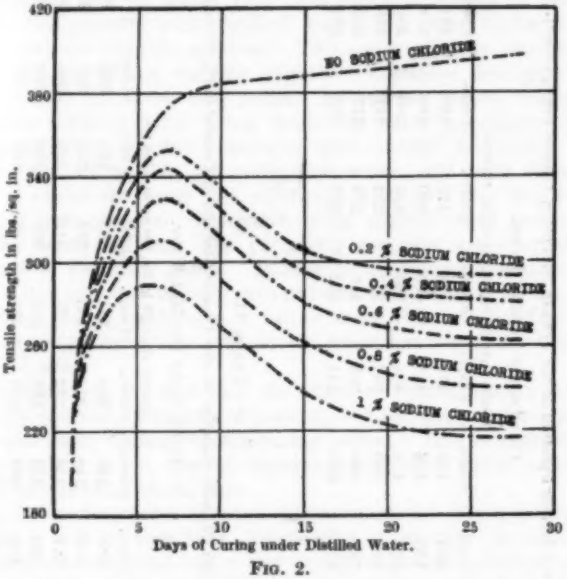

FIG. 2.

EFFECT OF SODIUM CHLORIDE SOLUTION ON THE TENSILE STRENGTH OF CEMENT (50 PER CENT. GAUGED WITH NaCl SOLUTION).

50 per cent. gauge grouts are collected in Tables I. and II., and are shown graphically in Figs. 1 and 2. It will be noticed that, for each gauge, the initial effect as shown by one day tests is to slightly increase the strength of the cement, the increment being greater as the percentage of chloride increases. After a few days the strength begins to decrease in every case where sodium chloride solution has been used for grouting, whereas if distilled water is used the cement continues to gain strength slowly. With 40 per cent. grouts the maximum strength is attained in from three to seven days; with 50 per cent. grouts the maximum strength is reached at

TABLE I.

Effect of Sodium Chloride Solution on the Tensile Strength of Cement (40% Grout).

Cured under Distilled Water.

Percentage NaCl in solution.	Tensile strength in lbs. per sq. in. after :—										
	1day.	3 days.	7 days.	8 days.	9 days.	10 days.	12 days.	13 days.	14 days.	15 days.	28 days.
Nil %	342	432	470	474	476	478	479	480	481	482	494
0·2%	351	420	436	428	418	409	390	380	374	368	350
0·4%	359	413	424	414	404	395	373	360	350	344	320
0·6%	365	405	410	399	387	377	353	341	329	320	288
0·8%	368	389	391	380	368	356	329	317	305	296	254
1·0%	370	380	370	360	344	332	305	292	284	275	235

TABLE II.

Effect of Sodium Chloride Solution on the Tensile Strength of Cement (50% Grout).

Cured under Distilled Water.

Percentage NaCl in solution.	Tensile strength in lbs. per sq. in. after :—										
	1 day.	3 days.	7 days.	8 days.	9 days.	10 days.	11 days.	12 days.	13 days.	14 days.	15 days.	28 days.
Nil %	194	312	376	382	383	384	385	385	385	386	388	398
0·2%	200	308	354	348	342	335	329	323	316	309	304	293
0·4%	209	300	344	338	332	325	319	312	306	300	294	280
0·6%	217	291	330	324	318	312	305	299	292	286	278	262
0·8%	225	283	310	304	298	292	285	280	273	266	260	240
1·0%	231	275	288	282	276	270	263	258	251	245	237	217

about seven days in every case. It will be evident from Figs. 1 and 2 that after attaining maximum strength the retrogression is rapid and, especially with 40 per cent. grouts, very persistent. The effect is so marked in the case of 40 per cent. grouts that, taking any particular concentration of sodium chloride solution, the tensile strength after 28 days is only slightly superior to that of the corresponding 50 per cent. grout. This is particularly true for the stronger sodium chloride solutions.

Turning now to Table III., this contains results of tests on briquettes grouted with distilled water, but cured under 0·6 per cent. sodium chloride solution. Two series of tests were carried out, the conditions varying slightly. Reference has previously been made to these two series. Briquettes placed under salt solution directly after being made up show a slightly higher strength after one day compared with similar briquettes which have been allowed to set under line water, and have then been placed under the same salt solution. After one day the reverse applies, retrogression of strength being slightly more pronounced in the former series. The preceding remarks apply equally to 40 and 50 per cent. grouts. It may be concluded, therefore, that salt water in a well coming into contact with cement, as the latter is being placed, will have a rather more deleterious effect than similar water contacting with cement which has been placed and has taken its set.

Summing up, we find that the effect of chlorides is to increase slightly the early strength of cement, but definitely to decrease its strength later during the hardening period. This retrogression is very marked in the case of cements mixed with water containing small proportions of chloride.

An interesting point arises in this connection. From the various Tables it will be seen that, irrespective of whether the cement is grouted with distilled water and cured under salt solution or vice versa, the maximum tensile strength will be reached within the first seven days. If then, in an ordinary well-cementing job, there is at any time contact between the cement and the well water (which normally will contain chlorine equivalent to a 0·6 per cent. sodium chloride solution), then obviously there is no point in allowing the cement to stand for more than about seven days before drilling out, since no increase in strength is to be expected as a result of prolonging the "shut-down" period.

Setting Time Tests.

Tables IV., V. and VI. contain results of tests made with 40, 50 and 60 per cent. gauge grouts respectively. Each table contains results of tests made under two different sets of conditions; in the

TABLE III.

Effect of Sodium Chloride Solution on the Tensile Strength of Cement Grouts.

Two series of experiments A and B are recorded. (A) Briquettes were made with distilled water, allowed to set under tap water and then place below 0·6% salt solution at 100° F. (B) Briquettes made with distilled water were placed below 0·6% salt solution at 100° F.

Series.	Percentage grout.	Tensile strength in lbs./sq. in. developed after :— 1 day.	3 days.	7 days.	8 days.	9 days.	10 days.	11 days.	12 days.	13 days.	14 days.	15 days.	28 days.
A	40%	354	416	435	431	426	420	415	409	405	399	395	372
B	40%	356	416	424	419	413	407	400	396	388	381	370	340
A	50%	201	308	348	348	346	344	342	339	336	330	328	316
B	50%	210	300	340	338	335	331	328	324	321	317	313	295

TABLE IV.

(a) 40% *Gauging with Water containing varying percentages of Sodium Chloride.*

(*Briquettes maintained in moist air at* 100° F.)

Determination.	% Sodium Chloride. Nil %. H. M.	0·2%. H. M.	0·4%. H. M.	0·6%. H. M.	0·8%. H. M.	1·0%. H. M.
Initial Set	2 33	2 28	2 23	2 18	2 15	2 10
Final Set	3 20	3 18	3 15	3 12	3 3	3 5
Decrease in Initial Set	—	– 5	– 10	– 15	– 18	– 22
Decrease in Final Set	—	– 2	– 5	– 2	– 12	– 15

(b) 40% *Gauging with Distilled Water and allowed to set under Water containing varying percentages of Sodium Chloride at* 100° F.

Determination.	% Sodium Chloride. Nil %. H. M.	0·2%. H. M.	0·4%. H. M.	0·6%. H. M.	0·8%. H. M.	0.1%. H. M.
Initial Set	2 35	2 30	2 25	2 20	2 18	2 12
Final Set	3 25	3 22	3 20	3 15	3 12	3 10
Decrease in Initial Set	—	– 5	– 10	– 15	– 17	– 23
Decrease in Final Set	—	– 3	– 5	– 10	– 13	– 15

TABLE V.

(a) 50% *Gauging with Water containing varying percentages of Sodium Chloride.*

(*Briquettes maintained in moist air at* 100° F.)

% Sodium Chloride.

Decrease in Final Set	—	– 5	– 10	– 15	– 17	– 23
		– 3	– 5	– 10	– 13	– 15

TABLE V.

(a) 50% *Gauging with Water containing varying percentages of Sodium Chloride.*
(*Briquettes maintained in moist air at* 100° F.)

Determination.	% Sodium Chloride.					
	Nil %.	0·2%.	0·4%.	0·6%.	0·8%.	1·0%.
	H. M.	H. M.	H. M.	H. M.	H. M.	H. M.
Initial Set	2 55	2 50	2 45	2 40	2 35	2 30
Final Set	3 45	3 43	3 40	3 33	3 35	3 30
Decrease in Initial Set	—	– 5	– 10	– 15	– 20	– 25
Decrease in Final Set	—	– 2	– 5	– 7	– 10	– 15

(b) 50% *Gauging with Distilled Water and allowed to set under Water containing varying percentages of Sodium Chloride at* 100° F.

Determination.	% Sodium Chloride.					
	Nil %.	0·2%.	0·4%.	0·6%.	0·8%.	1·0%.
	H. M.	H. M.	H. M.	H. M.	H. M.	H. M.
Initial Set	2 55	2 50	2 47	2 42	2 38	2 35
Final Set	3 50	3 47	3 45	3 40	3 37	3 32
Decrease in Initial Set	—	– 5	– 8	– 13	– 17	– 20
Decrease in Final Set	—	– 3	– 5	– 10	– 13	– 18

TABLE VI.

(a) 60% *Gauging with Water containing varying percentages of Sodium Chloride.*
(*Briquettes maintained in moist air at* 100° F.)

Determination.	% Sodium Chloride.					
	Nil %.	0·2%.	0·4%.	0·6%.	0·8%.	1·0%.
	H. M.	H. M.	H. M.	H. M.	H. M.	H. M.
Initial Set	3 40	3 35	3 30	3 25	3 20	3 15
Final Set	4 45	4 40	4 32	4 25	4 20	4 18
Decrease in Initial Set	—	– 5	– 10	– 15	– 20	– 25
Decrease in Final Set	—	– 5	– 13	– 20	– 25	– 27

(b) 60% *Gauging with Distilled Water and allowed to set under Water containing varying percentages of Sodium Chloride at* 100° F.

Determination.	% Sodium Chloride.					
	Nil %.	0·2%.	0·4%.	0·6%.	0·8%.	1·0%.
	H. M.	H. M.	H. M.	H. M.	H. M.	H. M.
Initial Set	3 30	3 25	3 22	3 18	3 15	3 12
Final Set	4 35	4 30	4 25	4 20	4 18	4 15
Decrease in Initial Set	—	– 5	– 8	– 12	– 15	– 18
Decrease in Final Set	—	– 5	– 10	– 15	– 17	– 20

first case the cement was grouted with water containing various percentages of sodium chloride, the test pats then being kept in moist air at 100° F., and in the second case the cement was grouted with distilled water and test pats were allowed to set under water

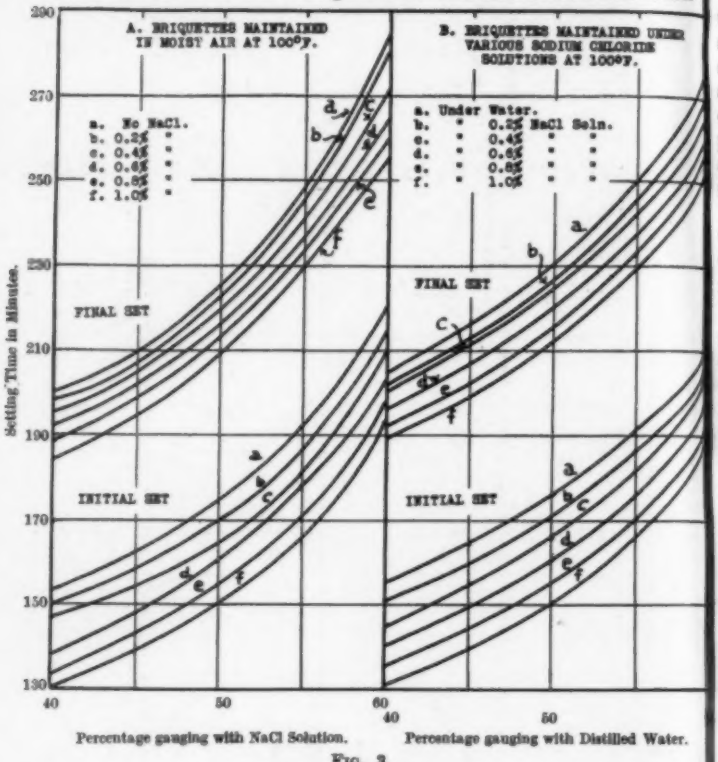

FIG. 3.

SETTING TIME OF VARYING GROUTS OF CEMENT. (A) GAUGED WITH SODIUM CHLORIDE SOLUTION AND ALLOWED TO SET IN AIR AT 100° F. (B) GAUGED WITH DISTILLED WATER AND ALLOWED TO SET UNDER SODIUM CHLORIDE SOLUTIONS.

containing various percentages of sodium chloride and maintained at 100° F. In every case a small decrease in the initial and final setting times was found as compared with corresponding times for pats grouted with and set under water. For any particular concentration of sodium chloride solution the decrease in the

setting time is about the same for the various gaugings. It will also be noticed that whereas with 40 and 50 per cent. grouts the initial set is affected slightly more than the final; the reverse holds good in the case of a 60 per cent. grout.

It is interesting to note that the observed setting times are about the same whether the cement is mixed with distilled water and then set under a sodium chloride solution, or mixed with the same sodium chloride solution and then set under distilled water. This seems to suggest that in the case of the test pats set under sodium chloride solution a fairly rapid diffusion of sodium chloride takes place from the solution into the test pat, the latter then being affected to much the same extent as a similar pat made up with sodium chloride solution.

The results discussed above are shown graphically in Fig. 3; the curves show plainly the progressive small decreases in setting time with increase in percentage of sodium chloride. It should be mentioned here that these results differ from those published by Uren (Petroleum Production Engineering, p. 280), who shows a graph connecting setting time of a 50 per cent. grout and percentage sodium chloride in the mixing water. According to this graph, all concentrations of sodium chloride up to 1·0 N. (*i.e.*, 5·85 per cent.) increase the setting time. With very dilute solutions (0·02–0·07 N. or 0·12–0·4 per cent. approx.) the setting time decreases, then with solutions up to about 0·15 N. or 0·88 per cent., it shows an increase, after which further additions of salt have little effect; actually there is again a slight decrease to a secondary minimum at 0·5–0·6 N. (3·0–3·5 per cent.) followed by a very slight increase up to 1·0 N.

Our results do not agree with these; it should be noted that while Uren obtains a slight decrease in setting time as the concentration of sodium chloride is increased from 0·12 to 0·4 per cent., his setting times are *always* longer than those with water, *i.e.*, his minimum setting time, which occurs at about 0·4 per cent. NaCl, is longer than the setting time with water.

Variation in Setting Time with Change of Temperature.—The setting times of cement grouts of various gauges at different temperatures have also been determined; in one series the cement was mixed with and set under distilled water, and in the second series mixed with distilled water and set under 0·6 per cent. sodium chloride solution. The results of these two series of tests are collected in Tables VII. and VIII., and are also shown graphically in Figs. 4, 5 and 6. From the figures given in the tables it will be seen that an increase in temperature of 10° F. results in a shortening of the initial setting time by about 15–20 minutes in the case of the grouts normally in use on the field.

TABLE VII.

Effect of Temperature on the Setting Time of Cement gauged with and set under Water.

% Gauging Water.	Determination.	100° F.		110° F.		120° F.		130° F.		140° F.		150° F.		160° F.	
		H.	M.	H.	M.	H.	M.	H.	M.	H.	M.	H.	M.	H.	M.
40%	Initial Set ..	2	33	2	15	1	50	1	32	1	20	1	5	–	50
	Final Set.. ..	3	20	2	55	2	30	2	10	1	50	1	30	1	10
50%	Initial Set ..	2	55	2	35	2	10	1	50	1	35	1	15	1	0
	Final Set.. ..	3	50	3	15	2	55	2	30	2	15	1	50	1	20
60%	Initial Set ..	3	30	3	5	2	40	2	20	1	50	1	22	1	5
	Final Set.. ..	4	35	3	55	3	25	2	55	2	20	1	55	1	27

TABLE VIII.

Effect of Temperature on the Setting Time of Cement gauged with Water and Set under 0.6% NaCl Solution.

% Gauging Water.	Determination.	100° F.		110° F.		120° F.		130° F.		140° F.		150° F.		160° F.	
		H.	M.	H.	M.	H.	M.	H.	M.	H.	M.	H.	M.	H.	M.
40%	Initial Set ..	2	20	2	5	1	40	1	25	1	10	–	58	–	42
	Final Set.. ..	3	15	2	50	2	20	1	55	1	35	1	20	1	–
50%	Initial Set ..	2	42	2	25	2	0	1	45	1	20	1	10	–	50
	Final Set.. ..	30	40	3	10	2	50	2	25	2	5	1	40	1	10
60%	Initial Set ..	3	18	2	55	2	30	2	5	1	45	1	15	1	0
	Final Set.. ..	4	20	3	40	3	20	2	45	2	15	1	48	1	20

In Fig. 1 the setting time solution cement. been "s curves a setting calibrate these te

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In Fig. 4 are given three series of curves, each series comparing setting times under water and under 0·6 per cent. sodium chloride solution at temperatures up to 160° F., for a definite gauge of cement. The curves are plotted from actual results and have not been "smoothed" out in any way. For any selected gauge the corresponding "under water" and "under 0·6 per cent. NaCl" curves are roughly parallel, the latter always showing the shorter setting time. The abscissæ of these curves, in addition to being calibrated in °F., also indicate the approximate depths at which these temperatures will be met.

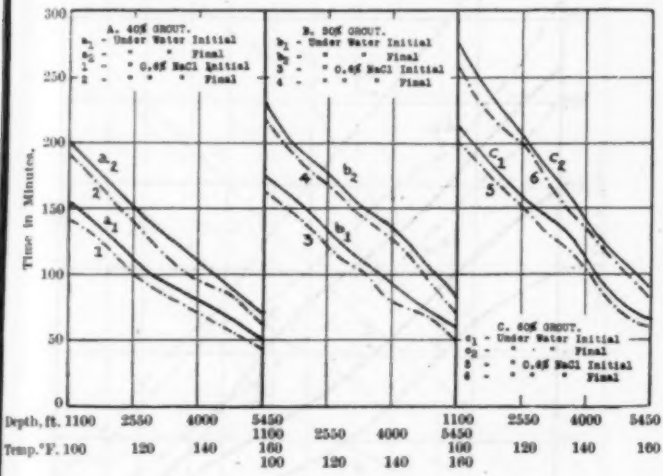

FIG. 4.

EFFECT OF TEMPERATURE ON THE SETTING TIME OF CEMENT. (A) UNDER WATER, AND (B) UNDER 0·6 PER CENT. NaCl SOLUTION.

The results are presented in a different manner in Figs. 5 and 6 The former compares the setting times of the different gauge grouts under water at various temperatures, and the latter shows the corresponding curves for setting times under 0·6 per cent. sodium chloride solution. These two graphs, therefore, show effect of dilution and of temperature on the setting time; it will be observed that at the higher temperatures the various initial (or final) curves tend to approach, *i.e.*, as the temperature increases, temperature, and not dilution, becomes the more important factor in determining the setting time.

Another point which may be demonstrated by means of these two graphs (Figs. 5 and 6) is in connection with the setting time of the cement in relation to the average time for a cement job.

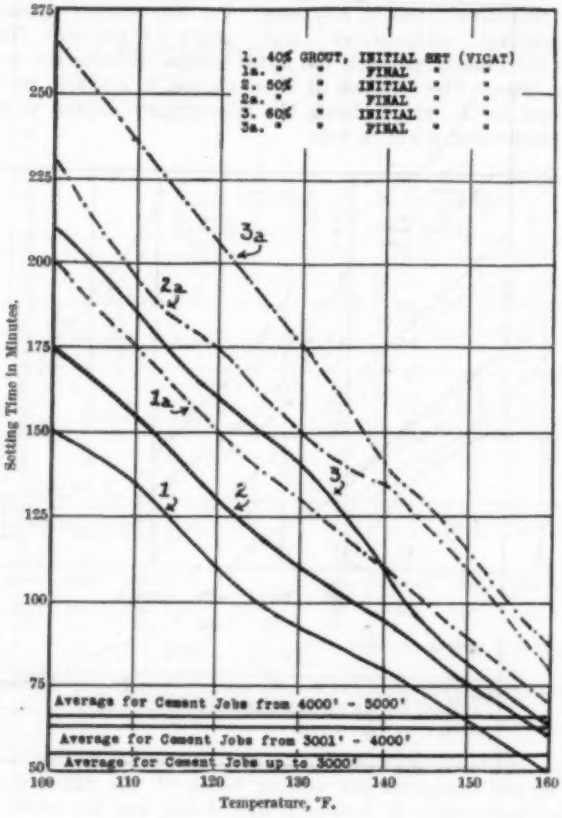
1. 40% GROUT, INITIAL SET (VICAT)
1a. " " FINAL " "
2. 50% " INITIAL " "
2a. " " FINAL " "
3. 60% " INITIAL " "
3a. " " FINAL " "
Setting Time in Minutes.
Temperature, °F.
Average for Cement Jobs from 4000' - 5000'
Average for Cement Jobs from 3001' - 4000'
Average for Cement Jobs up to 3000'

FIG. 5.

EFFECT OF TEMPERATURE ON THE SETTING TIME OF CEMENT (CEMENT GAUGED WITH WATER). (BRIQUETTES MAINTAINED UNDER WATER).

Average "mixing and displacing" times for cement jobs at various depths were assumed. Points were then taken on the time-axis of the curves, proportional to these average times, and lines drawn

from these points parallel to the abscissæ. An examination of the points of intersection of these lines with the setting time curves shows that theoretically even a 40 per cent. gauge grout can be

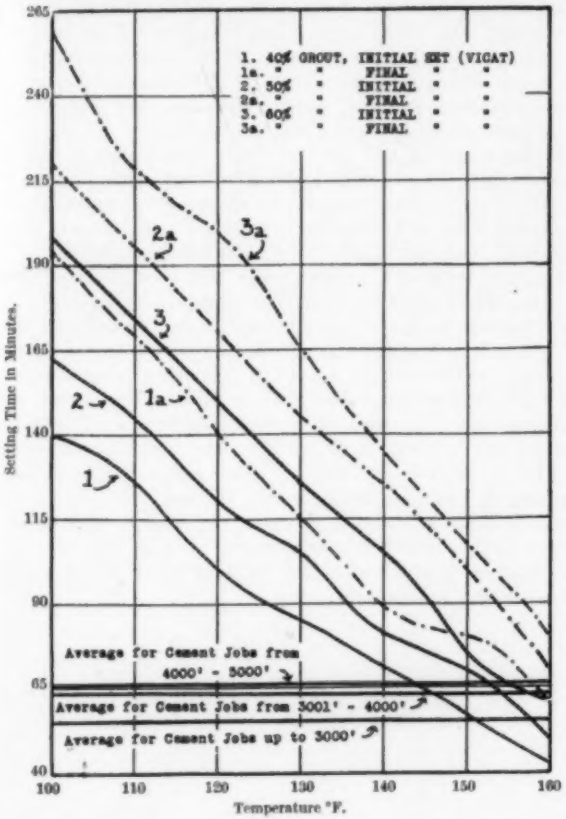

FIG. 6.

EFFECT OF TEMPERATURE ON THE SETTING TIME OF CEMENT (CEMENT GAUGED WITH WATER). (BRIQUETTES MAINTAINED UNDER 0·6 PER CENT. NaCl SOLUTION).

safely used where temperatures up to 140° F. exist (*i.e.*, to a depth of about 4000 ft.) without fear of the cement taking its initial set too early. This is true, even where the setting is accelerated by presence of salt solution (Fig. 6).

Conclusions.

The presence of sodium chloride either in the mixing water or in the medium under which cement sets, slightly increases the rate of hardening in the initial stages; this beneficial effect is, however, only of short duration, and is succeeded by a marked retrogression in the tensile strength of the cement. This decrease in strength is more evident if chlorides are present from the very first, *i.e.*, when they are present in the mixing water.

From the practical point of view this means that if well water containing chlorides in solution contacts with cement in the early stages, no benefit will be obtained by allowing the well to stand for more than a week before drilling out, since it is unlikely that the cement will continue to gain strength after that period.

The setting time of a cement grout will be slightly accelerated if the medium under which it sets contains small quantities of sodium chloride, as in the average well water for example, but this effect is not very marked and should not be a cause of trouble in the average well cementing job. It has been pointed out that, taking into consideration only the effect of chlorides and of temperature, no trouble should be experienced due to early setting of the cement in wells with bottom hole temperatures up to at least 140° F., even with 40 per cent. gauge grout. Since the percentage of water in the field mix is rarely, if ever, as low as 40 per cent., and considering also that the cement takes some time to attain the bottom hole temperature, then it may be assumed that difficulties of this nature are unlikely to occur on account of chlorides in the well waters.

Preparation of Paraffins from Carnuba Wax by Means of Catalytic Hydrogenation.*

By H. I. Waterman (Hon. Member), P. de Kok and A. J. Tulleners (Student).

The expelling of oxygen from Carnuba wax can quite easily be effected by means of high-pressure hydrogenation in the presence of several catalysts. Carnuba wax is mainly found in Brazil, in the form of a deposit on the leaves of a palm tree, and consists chiefly (over 45 per cent.) of myricylalcohol, $C_{30}H_{61}OH$, in the free and also in the ester state, as stated by Stürcke[1] and others. In addition, cerylalcohol, $C_{26}H_{53}OH$, cerotic acid, $C_{25}H_{51}COOH$, and smaller amounts of other higher alcohols, acids and hydrocarbons—*e.g.*, heptacosane, $C_{27}H_{56}$, have been found.

The wax under examination showed the following constants: Specific gravity, $^{81°\cdot1}/_{4°}$, 0·851; setting point, about 76° C.; saponification value, 86·0; acid value, 10·5; molecular weight (naphthalene as a solvent), 692; elementary analysis, 12·5 and 12·8 per cent. H (average 12·7), 79·2 and 79·3 per cent. C (average 79·2).

Two hydrogenations were carried out, one with molybdenum-carbon catalyst,[2] and the other with nickel-guhr catalyst.[3] To 400 g. of the wax were added 40 g. of the catalyst, an amount corresponding to 10 per cent. by weight of the wax. The temperature of the initial materials was raised by heating in a rotating Bergius autoclave, having a capacity of about 2 litres, the pressure at the beginning being somewhat above 100 kg./sq. cm.

Experiment I.—The temperature was allowed to rise slowly, the total period of heating occupying about 200 minutes. After 95 minutes the temperature was 300° C., and after 150 minutes 364° C., a maximum of 437° C. being obtained after 200 minutes. From the pressure-time curve it appears probable that the speed of hydrogenation, with the simultaneous formation of hydrocarbons, increased considerably at about 300° C. This temperature was determined with a thermocouple in a central tube and, therefore, differs from the temperature of the surrounding annular reaction tube on account of the fact that, starting from room

* Paper received October 11, 1932.

[1] *Ann.*, 1883, **223**, 283.

[2] E.P. 331,199. By accident the molybdenum catalyst had been mixed with a very small but unknown percentage of nickel catalyst.

[3] Waterman and Van Tussenbroek, *J.S.C.I.*, 1931, **50**, 227 T. The temperature of the reduction was maintained at 350° C. for 4 hours.

temperature, the heat is supplied externally. The product was removed from the autoclave when the reaction was completed, and the hydrogenated wax separated by melting and filtering at a temperature of 110° C. The colour, which was white at the start, soon turned to rose-brown, and the product appeared to be almost pure paraffin as the greater part of the oxygen must have been driven out, probably as water (see also Experiment II.). Although a considerable amount of the wax still remained adhering to the catalyst it was not recovered by extraction.

An analysis was made of the molten product only, with the following result: Quantity, 265 g.; specific gravity, $^{68°.4/4°}$, 0·7820; setting point, 57°–57°·5 C.; saponification value, 0; acid value, 0; molecular weight (naphthalene), 356[4]; elementary analysis, 14·5 and 14·3 per cent. H (average 14·4), 85·1 and 84·9 per cent. C (average 85), by difference 0.6 per cent. O; the bromine value (McIlhiney) was less than 3, so practically no bromine is absorbed; refraction at 68°·4 C.; n_c, 1·43374; n_D, 1·43618; n_F, 1·44167; n_G, 1·44625; specific refraction,

$$\frac{n_D^2-1}{n_D^2+2}\cdot\frac{1}{d}=0.3345;\ \text{Dispersion}\ \frac{n_G^1-n_c}{d}\times 10^4=160.$$

The specific refraction and the dispersion both indicate that the material is a pure paraffin. This is in agreement with the value of a pure paraffin as shown by the molecular weight-specific refraction curve from saturated hydrocarbons of a pure aliphatic character, namely, 0·3337.[5]

Experiment II.—In this experiment 400 g. of the wax were treated for 150 minutes under conditions similar to those of Experiment I., but nickel-guhr was used as the catalyst instead of molybdenum-carbon. The temperature was 200° C., 300° C. and 393° C. after 35, 65 and 135 minutes respectively, and was then allowed to fall to 330° C. after 140 minutes. Taking into consideration the difference between the temperature of the reaction chamber and the temperature of the measuring tube, as pointed out in Experiment I., the reaction became obvious at somewhat above 200° C. as far as could be judged from the pressure-time curve.

The resulting paraffin was bright white in colour and remained white after standing. Although there was no phenol-like smell as with the product of Experiment I., there was a disagreeable odour. Water was collected in the bottom of the autoclave and amounted to 10·2 g. The paraffin was harder than that of Experiment I., and was separated from the catalyst without the necessity

[4] 0·4286 g. paraffin dissolved in 9·568 g. naphthalene caused a depression of the freezing point of 0·873° C.

[5] Vlugter, Waterman and Van Westen, *Chem. Weekblad*, 1932, p. 226.

for melting and filtering. The amount removed from the catalyst by cutting was 170·5 g., and a further 104·0 g. was obtained from the residue. This was treated in the same way as described above. The amount which was still attached to the catalyst was 63·0 g. The analysis of the product was: Setting point, about 59° C.; molecular weight (naphthalene), 352, 356 (average 354)[6]; elementary analysis, 14·5 and 14·5 per cent. H. (average 14·5), 85·6 and 85·5 per cent. C. (average 85·5).

From the foregoing, the conclusion may be drawn that the conversion of a considerable amount of Carnuba wax into paraffin is possible without any breaking down worth mentioning. Excluding the amount which remained adhering to the catalyst, paraffin up to 70 per cent. by weight of the wax was obtained.

A comparison of the paraffin with industrial Rangoon paraffin is given in Table I., and it will be seen that there is agreement only to a certain extent. There is, however, no doubt that the high-pressure hydrogenation product of Carnuba wax is chiefly a pure paraffin.

TABLE I.

	Paraffin obtained from Carnuba was by catalytic high-pressure hydrogenation.		Rangoon paraffin.	
	I.	II.	H. A. Van Westen.[7]	J. N. J. Perquin.[8]
Setting point (Shukoff) ° C.	57·0–57·5	59	58	58
Specific gravity ..	0·7820 $^{68°}/_{4°}$	—	0·9157 $^{20°}/_{4°}$ 0·7744 $^{70°}/_{4°}$	0·913 $^{20°}/_{4°}$
Refraction, I. and II. at 68·4° C.; Rangoon at 70° C. n_c	1·4337	—	1·4312	1·4315
n_D	1·4362	—	1·4334	1·4336
n_F	1·4417	—	1·4388	1·4390
n_G	1·4462[2]	—	1·4432	1·4435
Dispersion	160	—	155	—
Specific refraction ..	0·3336	—	0·3359	—
Bromine value (McIlhiney)	<3	—	0	—
Mol. wt.	356	354	410[9]	422[9]
Elementary analysis. H %	14·4	14·5	—	14·75
C %	85·0	85·5	—	85·25

[6] 0·4939 and 0·8290 g. paraffin dissolved in 11·16 and 11·59 g. naphthalene respectively, caused a depression of the freezing point of 0·87° and 1·39° C.

[7] Dissertation, *Delft*, 1931, p. 86.

[8] Dissertation, *Delft*, 1929, p. 28.

[9] Camphor as solvent. Previous investigations, also with camphor, gave 417 and 427; this Jnl., 1932, **18**, 735-750.

CORRESPONDENCE.

To the Editor, November 1st, 1932.

Sir,—"**Improved Methods of Examining Mineral Oils,**" Vlugter, Waterman and van Westen, *J. Inst. Petr. Techn.*, 1932, **18**, 735–750.

In this very interesting paper, which I welcome as another attempt in the constitutional research work on lubricating oils, the authors criticise (p. 748) my paper (*Zeit. f. Physikal. Chem. A.*, 1929, **144**, 22) on the constitution of these oils.

The authors state that I classify valvoline oil as a mixture of isoparaffins, and that this is deduced from the absolute values of refractive index n_D and density d in connection with the molecular weight. A table is given by the authors to demonstrate by comparison of the specific refractions of some oils classified by me as isoparaffin mixtures with the specific refractions of the corresponding paraffins that my "conclusions are certainly incorrect."

As a physicist and physicochemist, and as stated in my paper in question and in a subsequent one (*Zeit. f. Physikal. Chem. A.*, 1931, **154**, 358–363), I based my classification on *all the physicochemical data available* at that time. This basis was rather broadened by the investigation on certain paraffin isomers by G. Edgar and G. Calingaert (*J.A.C.S.*, 1929, **51**, 1540), and in one point I agreed with my critic Bielenberg, that constitutional conclusions cannot be solely based on refractional data.

Referring to the table of the authors, p. 748, one misprint in my paper must be corrected first: the density of hydrocarbon "$C_{19}H_{36}$" is 0·8471 instead of 0·8771, and a misunderstanding of the authors: oil Ph. G. VI. is the German medical paraffin oil and not valvoline oil (Ph. G.=Pharmacopœa Germanica).

In the following table the *percentage* differences, referring to the data for the "corresponding paraffin," between the spec. refractions of the oils and the corr. par. are given first. Next follow the corresponding maximum percentage differences for some normal paraffins and some of their isomers, based upon the values given by Edgar and Calingaert.

	d_{20}	n_{20}^{D}	Spec. refr.	Δ	Δ%
Valvoline oil H. ..	—	—	0·3268	—0·0051	—2·54
"Corresp. paraffin"	—	—	0·3319		
Par. oil Ph. G. VI. ..	—	—	0·3216	—0·0116	—3·48
"Corresp. paraffin"	—	—	0·3332		
"$C_{16}H_{32}$"	—	—	0·3262	—0·0100	—2·98
"Corresp. paraffin"	—	—	0·3361		
"$C_{17}H_{36}$"	0·8471	—	0·3240	—0·0111	—3·31
"Corresp. paraffin"	—	—	0·3351		
"$C_{12}H_{26}$"	—	—	0·3458	+0·0079	+2·34
"Corresp. paraffin"	—	—	0·3379		
Hexanes :—					
n-Hexane	0·6595	1·3743	0·3460	+0·0023	+0·66
2·2 Dimethylbutane ..	0·6498	1·3700	0·3483		
Heptanes :—					
n-Heptane	—	—	0·3454	—0·0027	—0·78
3. Ethylpentane ..	—	—	0·3427		
Octanes :—					
n-Octane	0·702	1·3980	0·3436	—0·0016	—0·46
2. Methylheptane ..	0·6985	1·3935	0·3420		
2.2.3. Trimethylpentane	0·717	1·4184	0·3520	+0·0084	+2·45
Nonanes :—					
n-Nonane	—	—	0·3415	—0·0066	—1·93
4. Methyloctane ..	—	—	0·3349		

Comparison shows that these differences are roughly of the same order of magnitude and of varying sign, and that—if there can be anything said—their absolute values show rather an increase with increasing molecular weight. This appears, moreover, very probable from the molecular-physical point of view, because the probability of interaction between the atoms in the molecular greatly increases with the closer packing of side chains. The *absence* of such interaction, however, is a condition for any prediction on the value of the specific refraction of the molecule with increasing molecular weight. One might object that with the known isomers the differences are extreme values, whilst with the oils they are differences between *mixtures* and normal paraffins. This objection would not take into account (1) that in all probability for the above reason the comparable extremes in these higher molecular compounds will be greater, and (2) that, after all, the valvoline oils

are refined and *certainly* contain only a very small percentage of the normal paraffins, *i.e.*, just of the components with comparatively high specific refractions. So, if there can be anything said from refractional data in this case, the only thing is, that if these oils are mixtures of isoparaffins, they must in all probability have lower specific refractions than the corresponding normal paraffins.

Further, the authors state on p. 740, when dealing with naphthenes, that "isomeric hydrocarbons have equal specific refraction." Whilst this may be true for the examples given there, it should be remembered, that with complex side chains this statement must not necessarily be correct, as the data on the paraffin isomer show.

Some authors go still farther, *e.g.*, Davis and McAllister, who published a paper on the same subject as the present authors (not cited by them) in *Ind. Eng. Chem.*, 1930, **22**, 1326.

They simply base their system for determining the number of naphthene nuclei, etc., on the neglection of the "small differences" of n and d values of the paraffin isomers. Of course, after having thus excluded *ab initio* the possibility of discerning between isoparaffins and other compounds, as a matter of logical consequence, they cannot find them.

According to modern conceptions of the nature of chemical linkage and compounds, as far as I can see, the only objection that can be made to my identification of the oils in question as isoparaffins is that such a conclusion seems trivial, because where there are normal paraffins present and left for geological ages under geological conditions, they must establish an equilibrium with all their possible isomers for reason of their close relationship and the low values of their heats of transformation.

S. KYROPOULOS.

Baurat Gerberstr., 7,
Göttingen.

To the Editor. November 11th, 1932.

Sir,—We have studied with great interest the remarks of Dr. Kyropoulos concerning our paper. According to his opinion the fact that Pennsylvania oils possess a specific refraction, which deviates from that of the normal paraffins, serves as proof of the isoparaffinic character of these oils. We are aware of the fact that the specific refraction of isomeric hydrocarbons is not absolutely constant, but we have to consider mean values and not the maximum deviations. These mean values are always very near to those of the normal paraffins. Let us also take as a basis the investigation of G. Edgar and G. Calingaert.

Hexanes.	$d^{20}/_4$	n_D^{20} (calc.).	$\frac{n^2-1}{n^2+2}\frac{1}{d}$	Average value.	Calculated from atomic refractions.
n. Hexane	0·6595	1·3738	0·3461		
2 Methylpentane	0·6542	1·3722	0·3476		
3 Methylpentane	0·6647	1·3771	0·3461	0·3473	0·3473
2.2 Dimethylbutane	0·6498	1·3694	0·3476		
2.3 Dimethylbutane	0·6618	1·3787	0·3489		
Heptanes.		n_D^{20}.			
n. Heptane	0·6836	1·38777	0·3450		
2 Methylhexane	0·6789	1·38509	0·3453		
3 Methylhexane	0·6870	1·38873	0·3441		
3 Ethylpentane	0·6984	1·39366	0·3422		
2.2 Dimethylpentane	0·6737	1·38233	0·3457	0·3440	0·3448
2.3 Dimethylpentane	0·6952	1·39201	0·3425		
2.4 Dimethylpentane	0·6745	1·38233	0·3453		
3.3 Dimethylpentane	0·6934	1·39114	0·3428		
2.2.3 Trimethylbutane	0·6900	1·38940	0·3431		
Octanes.					
n. Octane	0·702	1·3980	0·3438		
2 Methylheptane	0·6985	1·3935	0·3421		
3 Methylheptane	0·707	—	—		
4 Methylheptane	0·722	1·398	0·3343		
3 Ethylhexane	0·713	1·4016	0·3412		
2.3 Dimethylhexane	0·720	1·4093	0·3436	0·3433	0·3431
2.4 Dimethylhexane	0·703	1·4026	0·3468		
2.5 Dimethylhexane	0·696	1·3929	0·3428		
3.4 Dimethylhexane	0·721	1·4058	0·3405		
2 Methyl 3 ethylpentane	0·704	1·4016	0·3456		
2.2.3 Trimethylpentane	0·717	1·4184	0·3518		
2.2.4 Trimethylpentane	0·6918	1·3916	0·3439		

The underlined compounds have been chosen by Kyropoulos. We do not understand why he took these compounds and not others. Furthermore, the purity of some of these compounds is questionable. It is not clear why his products should contain isoparaffins with comparatively low specific refraction and high index of refraction,

as these properties are characteristic for naphthenes. From elementary analyses we have in no case found appreciable deviation in specific refraction with paraffin-base oils of high molecular weight. We draw attention to the fact that for aromatic-free oil elementary analyses can be calculated from experimentally found specific refractions. We always found good agreement with elementary analyses actually carried out. If the oils in question were isoparaffins the elementary analyses should give the formula C_nH_{2n+2}, which in reality is not the case.

We therefore maintain our opinion that Kyropoulos' identification of the Pennsylvania oils as isoparaffins is not right.

We knew the interesting paper by Davis and McAllister.[1]

J. C. VLUGTER, H. I. WATERMAN and
H. A. VAN WESTEN.

Delft,
The Technical University,
(Holland).

[1] Compare J. C. Vlugter, Thesis Delft (Holland), 1932. The conclusions of Davis and McAllister do not agree with those of Kyropoulos. They conclude that Pennsylvania type oils (saturated hydrocarbons) are composed essentially of a grouping of paraffin chains with naphthene rings, whereas Kyropoulos lists the Pennsylvania oils as isoparaffins.

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